Impurity Green’s function in the five frequency model of diffusion in the FCC host: General case and the limit of strong impurity-vacancy binding

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The impurity Green’s function exact to the first order in the vacancy concentration has been calculated in the framework of the five frequency model (5FM). The solution in terms of determinant ratios has been obtained with the use of the Cramer’s rule. The determinant sizes varied from 54 for the most general case to three for the four frequency model. Both analytical and numerical techniques has been used to analyze the solution. Special attention has been devoted to the case of strong impurity-vacancy (I-v) binding in order to substantiate the picture of diffusion via bound I-v pairs developed earlier in a phenomenological approach. Complete agreement with the phenomenological theory has been established thus providing its rigorous justification. The solution has been also applied to the calculation of the diffusional broadening of the Mössbauer resonance in FeAl system and good agreement with available experimental data and calculations within the encounter model has been found. The decay of the density of the nearest neighbor I-v pairs has been discussed in detail and suggested to be used as an additional constraint on the parameters of the 5FM. The possibility of experimental observation of the decay with the use of the positron annihilation technique has been pointed out.

I. INTRODUCTION

In Ref. 1 (in the following referred to as I) the impurity Green’s function (GF) of the five-frequency model (5FM) of the vacancy-mediated diffusion was calculated in the limit of a strong impurity-vacancy (I-v) attraction. The solution was based on the phenomenological approaches of Refs. 4 and 5 where the bound I-v pairs were treated as quasiparticles which diffusion was shown to be responsible for the non-Gaussian diffusion profiles (NGDPs) and the non-Fickian diffusion experimentally observed in the bulk diffusion in silicon and in the Cu(001) surface layer. Because of the instability of the bound pairs, the diffusion proceeds via repeated I-v associations and subsequent decays with the encounters separated by long periods of immobility because of the low vacancy concentration that usually does not exceed 0.1 at.% even at the melting point. After large number of encounters the impurity density distribution acquires the conventional Gaussian shape but at the early stage of diffusion it exhibits the exponential-looking tails characteristic of a defect-mediated diffusion.

In I the phenomenological approach was implemented within the 5FM with the model parameters taken from the first-principles calculations of Refs. 11 and 12 and the universal NGDPs were simulated. However, in Refs. 3, 10, 14 and 15 it was shown both theoretically and experimentally that for the existence of exponential profiles the I-v attraction is not indispensible and may occur even under the I-v repulsion. Furthermore, the picture of bound I-v pairs diffusing at distances much larger than the lattice constant does not accord well with the numerical simulations of Ref. 18 where despite rather strong I-v binding (0.29 eV) the I-v encounter amounted on average to only two exchanges between the impurity and the vacancy before their separation. This is only 50% more than the tracer-vacancy exchanges in the self-diffusion with no I-v attraction. So the question arises about the uniqueness of interpretation of NGDPs in terms of the pair diffusion and of interrelation of this mechanism with the alternatives that do not require I-v attraction, as well as of the ways of making distinction between them.

The aim of the present paper is to justify the pair diffusion picture suggested in I within a rigorous master equation and Green’s function formalism. Our approach will be based on generalization of the technique developed in Refs. 18 and 19 for the cases of self-diffusion and of the diffusion in a two frequency model. The method of solution that will be developed in the present paper can also be applied to diffusion in any elemental crystalline hosts and to more complex models with further than nearest neighbor (NN) vacancy jumps and with arbitrary but finite I-v interaction range. Such extensions has been suggested in literature on the basis of physical arguments and the first-principles calculations.

The text of the paper is organized as follows. In the next section an infinite system of rate equations for the impurity GF accurate to the first order in the vacancy concentration will be derived; in Sec. III it will be reduced to a finite system of 54 equations amenable to solution by Cramer’s rule. In Sec. IV the solution will be used for illustrative calculation of the diffusional broadening of the Mössbauer resonance and for discussion in this context of the encounter model (EM). In Sec. V the finite system obtained in Sec. III will be further reduces to the system of 13 equations which are sufficient for the study of macroscopic diffusion. In Sec. VI the diffusion constant and the parameters of the tightly bound I-v pairs will be studied numerically to confirm the analytic expressions derived in the phenomenological approach. In Sec. VII the complications that arise in the case of I-v interaction of arbitrary strength will be discussed and a
simpler four frequency model (4FM) that makes possible explicit analytic solution for impurity GF will be introduced. Dissociation of NN pairs which may be present in the initial state will be discussed in detail and a possibility of experimental measurement of the evolution will be suggested. It will be shown that the data on the NN density evolution can provide additional information about the values of the 5FM parameters. In final Sec. VII the main results will be briefly summarized.

II. RATE EQUATIONS FOR THE IMPURITY GF

In the 5FM all interactions in the system comprising the host crystal, the solute impurities, and the vacancies are reduced to interactions within one I-v pair.

Hence, the physics that the model can describe is that of diffusion in a dilute alloy where each impurity can be treated independently, so theoretical consideration can be restricted to only one of them. Because during one I-v encounter the impurity is displaced only on a microscopic distance, for macroscopic diffusion a large number of repeated encounters is necessary. Therefore, the “minimal model” that will be studied below is a host crystal consisting of $N \to \infty$ sites containing one substitutional impurity and $c_v N$ vacancies distributed within the crystal with concentration $c_v \ll 1$. The large number of vacancies makes the problem a truly many-body one. However, the interactions of impurity with two and more vacancies would be very different from the simple superposition of independent I-v interactions and would require a large number of additional parameters to be introduced, such as the values of multi-vacancy interactions. This would strongly diminish the usefulness of the model so in the absence of adequate description of the impurity interacting with more than one vacancy the physically meaningful solution should not go beyond the pair I-v interactions. This reduces the task to essentially a two-body problem that can be solved exactly. Such a solution will be presented below and from a physical point of view it may be considered as the best possible one because it cannot be improved further without redefinition of the model.

Because 5FM is a stochastic model, it can be exactly described by a suitable master equation (ME) (see Ref. 27 and Appendix A). Its direct solution, however, usually is efficient only in the case of a few-body system, like the bound two-particle I-v pair treated in I with the use of ME. In the case of the infinite number of vacancies a straightforward use of ME would require dealing with the coordinates of all $c_v N = O(N)$ vacancies in the system which is superfluous and practically unfeasible. An appropriate way of proceeding is to average over positions of all vacancies that do not participate in the I-v encounter. This can be achieved within the rate equations (REs) approach which is, in fact, a method of solution of the ME, as explained in Appendix A.

To derive the necessary REs let us define the impurity GF $G_I(t)$ as the probability density of finding the impurity at time $t$ at the lattice site described by vector $l$ with the integer coordinates $(l_X, l_Y, l_Z)$ if at time $t = 0$ it was located at site $0 = (0, 0, 0)$

$$G_I(t = 0) = \delta_{l0}. \quad (1)$$

This choice of the initial position was made for convenience because GF for arbitrary initial position $l'$ can be trivially obtained by the substitution $I \to 1 - I'$.

To express GF as a statistical average let us introduce the occupation number $\hat{i}_l$ which is equal to unity when site $l$ is occupied by the impurity and is zero otherwise. In this notation

$$G_I(t) = \langle \hat{i}_l \rangle \quad (2)$$

where the angular brackets denote the average over the time-dependent nonequilibrium statistical ensemble defined in Eq. (A5). Thus, besides $c_v N$ vacancies the ensemble contains the inhomogeneous impurity density distribution $G_I(t)$. The evolution continues until the impurity occupies all sites of the crystal with equal probability $1/N$ in which case the density gradient vanishes and the macroscopic diffusion ceases.

Because the I-v exchanges are restricted only to NN sites, the rate of change of the impurity density on site $l$ is determined solely by the I-v configuration on this site and its NNs. Thus, the average impurity density at site $l$ may grow when the site is occupied by a vacancy while the impurity occupies one of the NN sites, so that the impurity can jump at the vacant site by the I-v exchange and the density may diminish when site $l$ is occupied by the impurity and there is a NN vacancy for the impurity to leave the site. The exchanges occur with frequency $w_2$ and their rates are proportional to the joint probability density of simultaneous presence of the I-v pair at the NN sites as

$$\frac{d}{dt} G_I(t) = \frac{d}{dt} \langle \hat{i}_l \rangle = w_2 \sum_e [\langle \hat{i}_{l+e} \hat{i}_l \rangle - \langle \hat{i}_l \hat{i}_{l+e} \rangle] = w_2 \sum_e [\rho_{l+e}(t, -e) - \rho_l(t, e)], \quad (3)$$

where $e$ is the set of 12 vectors connecting NN sites in the FCC lattice and $\hat{i}_l$ is the vacancy occupation number. The joint pair probability density is defined as

$$\rho_l(t, n) = \langle \hat{i}_l \hat{i}_{l+n} \rangle, \quad (4)$$

where $n$ is the relative position of the vacancy with respect to the impurity at site $l$; the time dependence on the right hand side (r.h.s.) is implicit in the nonequilibrium average Eq. (A5).

Thus, as could be expected on the basis of the general rate equation Eq. (A9), the time derivative of the average impurity density $\langle \hat{i}_l \rangle$ in Eq. (3) depends on the average
densities in Eq. (4) so to solve Eq. (3) further REs need be derived. Fortunately, it is easy to see that to the first order in the vacancy concentration the chain of the REs terminates already at the equation for the joint probability density $\rho$. Indeed, because there is only one impurity in the system, higher order correlation functions may contain only additional vacancy occupation numbers. But then they will be of higher order in $c_v$ and thus can be omitted in the $O(c_v)$ approximation.

The second (and the last in the approximation chosen) RE reads

$$\frac{d}{dt} \rho_l(t, n) = w_2 \sum_e \delta_{ne} [\rho_{l+e}(t, -e) - \rho_l(t, e)] + \sum_{e} w_{n+e,n} \rho_l(t, n + e) - \left( \sum_{e} w_{n,n+e} \right) \rho_l(t, n). \tag{5}$$

It is derived as follows. By the chain rule, the time derivative on the r.h.s. of Eq. (4) should consist of two contributions: one corresponding to the change in the impurity density and the other one in the vacancy density. Therefore, the first line on the r.h.s. of Eq. (5) should coincide with the r.h.s. of Eq. (3) only corrected by the factor $\delta_{ne}$ to account for the fact that the impurity can move only when the only available vacancy at $n$ is at a NN site to the impurity. Similarly, the second line describes the diffusion of a vacancy and formally has the same structure as the equation for the free vacancy diffusion in Appendix B but with an important difference that the jump frequencies are not all equal to $w_0$ but depend on the vacancy position with respect to the impurity and on the jump direction, as defined in the 5FM (see, e.g., Fig. 1 in I). In matrix notation it can be described with the use of matrix $W$ having the same structure as matrix $W^0$ in Eq. (12) but instead of $-12w_0$ at the matrix diagonal in $W^0$ $W$ should contain the sum of all jump frequencies from site $n$ to the 12 NN sites (the negative term on the last line of Eq. (5)) while the positive term should include frequencies of all possible vacancy jumps from the sites that are NN to $n$ to this site (in $W^0$ they are all equal to $w_0$).

As is seen, the equation for the rate of change of the pair density $\rho_l$ in $O(c_v)$ approximation depends only on the pair density itself. So the density evolution can be found from this equation alone, provided the initial condition is known. With the initial location of the impurity at the coordinates origin, it remains to chose the initial distribution of the vacancies. In principle, in an out-of-equilibrium system the distribution can be arbitrary. But in order to describe the evolution towards thermal equilibrium one would need to know in detail the vacancy kinetics. For example, if the vacancies are in excess in comparison with the equilibrium concentration than in order to describe such phenomena as the creation of divacancies, vacancy pores, or dislocation loops one would need to know intervacency interactions. Besides, both under the vacancy excess or deficit their sources or sinks must be introduced into the model in order to correctly describe the kinetics leading to the equilibrium. Such terms, however, are absent in the 5FM, so the model implicitly presumes the vacancy concentration to be a constant parameter independent of the kinetics. This is possible only at thermal equilibrium. This reasoning, however, is valid only for the global vacancy concentration while a local distribution in the vicinity of the impurity still can be arbitrary. The local density perturbation concerns only $O(1)$ number of vacancies which cannot influence global concentration $c_v$ in the thermodynamic limit. But to further simplify the problem, in the present paper we will restrict our consideration to the simplest symmetric distribution. Namely, we assume that at $t = 0$ the vacancies are distributed homogeneously everywhere in the crystal with the equilibrium density $c_v$ except at the site occupied by the impurity where the density should be zero by the vacancy definition and at the sites NN to the impurity where the concentration $c_{NN}$ is assumed to be different from $c_v$ because, e.g., of the I-v interaction. These conditions are satisfied by the expression

$$\rho_l(t = 0, n) = \delta_{0l} \left[ c_v - c_v \delta_{n0} + (c_{NN} - c_v) \sum_e \delta_{ne} \right], \tag{6}$$

where the first factor on the r.h.s. accounts for the initial impurity position.

The initial value problem for a linear equation with constant coefficients can be conveniently solved by means of the combined integral Laplace and Fourier transform (the LF-transform) that for an arbitrary function $\phi$ can be defined as

$$LF[\phi_l(t)] = \phi(K, z) = \int_0^\infty dt \ e^{-zt} \sum_l e^{-i\alpha K l/2} \phi_l(t). \tag{7}$$

Under the transform Eq. (5) becomes

$$z \rho(K, z, n) = c_v - c_v \delta_{n0} + (c_{NN} - c_v) \sum_e \delta_{ne} + w_2 \sum_e \delta_{ne} e^{i\alpha K e/2} \rho(K, z, n) - \rho(K, z, n) \tag{8} + \sum_e w_{n+e,n} \rho(K, z, n + e) - \left( \sum_e w_{n,n+e} \right) \rho(K, z, n),$$

where

$$\rho(K, z, n) = LF[\rho_l(t, n)]. \tag{9}$$

The first line on the r.h.s. in Eq. (8) is the Fourier transformed initial value of the pair density Eq. (6). The remaining two lines originate from the first and the second lines on the r.h.s. of Eq. (4). Thus, for each $K$ we obtain an infinite inhomogeneous system of equations for the $N$-dimensional vector $\tilde{\rho}_K$ with components

$$\tilde{\rho}_K|_n = \rho(K, z, n) \tag{10}$$

which in the thermodynamic limit becomes infinite-dimensional. In the next section it will be shown that if the jump rates $w_{n,m}$ in Eq. (8) differ from the bulk
rate $w_0$ only within a finite region around the impurity, the infinite set of equations can be reduced to a finite linear system.

To conclude this section let us derive an expression for the impurity GF in terms of the solution of Eq. (8). The LF-transformed Eq. (8) reads

$$zG(K, z) = 1 - w_2 \sum \rho(K, z, e),$$

(11)

where use has been made of the fact that summations over $e$ and $-e$ are equivalent due to the lattice symmetry. Casting Eq. (11) in the form

$$G(K, z) = \frac{1}{z - \Sigma(K, z)},$$

(12)

where

$$\Sigma(K, z) = -w_2 \sum (1 - e^{-iK \cdot e/2})z \rho(K, z, e),$$

(13)

is the diffusion kernel, one can recognize in Eq. (12) the first two terms of the expansion of of the GF in the Dyson form

$$G(K, z) = \frac{1}{z - \Sigma(K, z)},$$

(12)

as discussed in Sec. IV in I. In the theory of vacancy-mediated diffusion Eq. (14) can also be obtained in the rate equation approach. In Appendix C we show that it can be rigorously derived in the framework of the Mori-Zwanzig memory-function formalism. But the equations for the memory function (or the self-energy) that can be obtained from Eq. (14) become useful mainly in high order expansions where they significantly reduce the number of contributions by restricting them only to irreducible ones. The lowest order terms that we are interested in is easily recoverable from the much simpler REs for GF.

III. SOLUTION OF THE RATE EQUATIONS BY THE CRAMER’S RULE

The method of solution presented below is a generalization to the case of the 5FM of the method suggested in Refs. 18 and 19 for the cases of self-diffusion and for the impurity diffusion in a two-frequency model. As will be seen, the method can be applied to any model with I-v interactions of finite range. Its essence is the reduction of the infinite (in the thermodynamic limit) set of equations Eq. (8) to a finite linear system.

To begin with, we note that one component of $\dot{\rho}_K$ can be found immediately. Examination of Eq. (8) shows that $\rho(K, z, n = 0) = 0$ satisfies the equation independently of the values of other components of $\dot{\rho}_K$. Indeed, only the terms on the third line on the r.h.s. of Eq. (8) could potentially cause problems. But because simultaneous presence of the vacancy and the impurity at the same site are forbidden, the jump rates to- and from the impurity site must be set equal to zero

$$w_5 = w_{e,0} = w_{0,e} = 0.$$  

(15)

Here the fictitious sixth frequency $w_5 = 0$ was introduced in order to formally treat the jumps between all sites on the same grounds. Thus, $\rho(K, z, n = 0) = 0$ satisfies Eq. (8) and later will be excluded from consideration.

Our next step is to subtract from both sides of Eq. (8) vector $\dot{\rho}_K$ with the components

$$\dot{\rho}_K^0 = \sum \dot{\rho}_n^0 \rho(K, z, m),$$

(16)

where $\dot{\rho}_K^0$ is the matrix from Eq. (B2) that describes the vacancy diffusion in the pure host crystal. The last line in Eq. (8) has similar formal structure and can be written down as $\dot{\rho}_K^0$ so that after the subtraction the terms on the line become

$$(\dot{W} - \dot{W}_0)\dot{\rho}_K.$$  

(17)

Because beyond the forth coordination shell (CS) the rates in $\dot{W}$ are equal to those of $\dot{W}_0$ (see the discussion following Eq. (5)), the matrix difference in Eq. (17) has nonzero matrix elements only for $m, n$ in a vicinity of the impurity. This means that Eq. (17) contains only a finite number of components of $\dot{\rho}_K$. Taking into account that $\dot{\rho}_K^0(n)$ on the second line in Eq. (8) are restricted to the first CS, the number of the vector components on the r.h.s. of Eq. (8) is also finite.

As can be seen from the definition of the 55FM and from Eq. (1) there are 54 sites in four CSs plus one site at $n = 0$ (55 in total). In matrix notation the equation can now be written as

$$(z - \dot{W}_0)\dot{\rho}_K = \dot{c}_0 + V \dot{\rho}_K,$$

(18)

where in the $55 \times 55$ matrix $V$ we gathered all matrix elements of Eq. (17) and also the terms on the second line of Eq. (8). The inhomogeneous term is the vector composed of the terms on the first line of Eq. (8)

$$\dot{c}_0|_n = c_v - c_v \delta_{n0} + (c_{NN} - c_v) \sum \delta_{ne}.$$  

(19)

However, on the l.h.s. of Eq. (18) all components of the vector $\dot{\rho}_K$ are still present after the subtraction:

$$(z - \dot{W}_0)\dot{\rho}_K.$$  

(20)

The components are mutually coupled because of the structure of matrix $\dot{W}_0$ in Eq. (12) which always connects the vector components in a given CS to higher CSs. To overcome this difficulty, let us multiply both sides of the equation by the matrix

$$\dot{P} = (z - \dot{W}_0)^{-1} = [P_{n - n'}]$$  

(21)
The GF obtained from the solution of the 54 equations Eq. (23) can be used to describe situations where large values of momentum $\mathbf{K}$ are of interest, which will be illustrated in the next section.

IV. DIFFUSIONAL BROADENING OF THE MÖSSBAUER LINE

An important advantage of the rigorous solution for the impurity GF is that it is not restricted to small values of the Fourier momentum as the phenomenological GF but is valid for arbitrary $\mathbf{K}$. This makes possible theoretical description of such techniques as the quasielastic neutron scattering, the coherent X-rays and the Mössbauer spectroscopies.

As an illustrative example let us consider the diffusional broadening of the Mössbauer line in the FeAl system studied in Ref. 16. The system is interesting from the point of view of the pair diffusion because of the rather strong I-v attraction of 0.29 eV as estimated from the experimental data. However, the diffusion profiles simulated on the basis of the extracted 5FM parameters were found to be roughly Gaussian (see Fig. 3 in Ref. 16). Furthermore, some other conclusions drawn by the authors do not agree with the results obtained in I, so below we will attempt to clarify these issues.

Diffusional behavior contributes to the Mössbauer broadening through the van Hove correlation function which at small impurity concentrations coincides with the single impurity GF calculated in Sec. III. In the Mössbauer studies it was found that the line broadening can be adequately described in the framework of the EM, so we first establish connection of our approach with the EM. To this end we note that an important parameter of the EM is the average number of steps $z_{\text{enc}}$ that the impurity makes during one I-v encounter. Physically $z_{\text{enc}}$ is akin to the mean diffusion distance $\lambda$ of the phenomenological theory and establishing a formal relationship between the parameters should facilitate comparison between two approaches.

Formally the diffusion contribution to the Mössbauer line broadening is given by the real part of the impurity GF at $z = \gamma/2 + \omega$, where $\gamma$ is the natural width of the Mössbauer line and $\hbar \omega$ is the energy transferred to the system by the gamma ray, so our solution for the GF should be sufficient for the task. However, in Refs. 16 and 24 it was pointed out that the solutions of the kind of our Eq. (11) cannot be directly compared with experimental Mössbauer spectra because the measured quantity is the width of the line which can be accurately fitted by the Lorentzian distribution. But the line shape in Eq. (14) is not Lorentzian because of the $z$-dependent diffusion kernel $\Sigma$. The difficulty is overcome by the EM that describes the diffusion as a sequence of repeated I-v encounters. In the course of the encounter a vacancy is always present in the vicinity of the impurity so all impurity jumps occur within a short time inter-
val $\Delta t_{\text{enc}} = O(1)$ which is small in comparison with the
time interval between the encounters that is equal to the
association time

$$t_a = g^{-1} = O(c_w^{-1}) \gg \Delta t_{\text{enc}}.$$  \hfill (25)

So to a good approximation $\Delta t_{\text{enc}}$ can be neglected on
the scale of $t_a$ and the impurity transfer during the en-
counter from the initial to the final position may be con-
sidered as instantaneous. This picture can be translated into the following approximation to GF. The diffusion equation satisfied by GF in Eqs. (14) and (C16) under the inverse LF-transform would read

$$\partial G(t)/\partial t = \int_0^t dt' \sum_{\nu} \Sigma_{\nu}(t')G_{1-\nu}(t-t') .$$  \hfill (26)

Because $\Sigma$ varies on the time scale $O(\Delta t_{\text{enc}})$ which is much shorter than $t$, the self-energy will differ from zero only in a narrow region of its argument where $t' \ll t$ so in the argument of $G$ in Eq. (26) $t'$ can be neglected: $t-t' \approx t$. Now the integration over $t'$ reduces to multiplication of GF at time $t$ by $\int_0^t \Sigma(t')$ where the upper limit can be safely extended to infinity. \(^{24}\) But such integration is equivalent to $z = 0$ component of the Laplace transform of $\Sigma$, so the LF-transformed GF in this approximation will be

$$G^{\text{enc}}(K, z) = \frac{1}{z - \Sigma(K, 0)}$$  \hfill (27)

(the correction due to the natural line width $\gamma$ was found to be negligible in the experimental conditions of Ref. \(^{16}\)). In this approximation the real part of GF becomes a Lorentzian of width \(^{24}\)

$$\Delta \Gamma = -2\Sigma(K, 0) ,$$  \hfill (28)

and is a real non-negative function of $K$.

The quantity \(^{16}\)

$$\Delta_{\text{LW}}(K) = \Delta \Gamma/|K| = -2\Sigma(K, 0)/|K|$$  \hfill (29)

with $K$ corresponding to the Mössbauer gamma rays and with $\Sigma$ from the Cramer’s rule solution of Sec. III has been calculated and smeared with the experimental resolution. In Fig. 2 the curve thus obtained is compared with the experimental data and the Monte Carlo (MC) simulations of Ref. \(^{16}\). The same parameters of the 5FM were used in the calculations with a minor correction for $w_2$ which was reduced by 4% to account for the fact that in the MC simulations the correlation factor was estimated as $f = 0.92$ while Eq. (50) gives $f = 0.96$. So $w_2$ was modified for the calculated diffusion constant agreed with the fit to experimental data. \(^{16}\)

In the EM the momentum-dependent line broadening was found to be (see Eqs. (6) and (7) in Ref. \(^{23}\))

$$\Delta \Gamma = \frac{2}{\tau_{\text{enc}}} (1 - W^{\text{enc}}(K)) ,$$  \hfill (30)

where $W^{\text{enc}}$ is the Fourier transform of the distribution of the impurity density over the lattice sites after the I-v encounter with $\tau_{\text{enc}}$ being the average time between the encounters. In the phenomenological approach similar expression can be obtained by substituting Eq. (D3) from Appendix D into Eq. (28):

$$\Delta \Gamma = 2g \left(1 - \frac{1}{1 + (\lambda|K|)^2}\right) .$$  \hfill (31)

In the phenomenological approach $\tau_{\text{enc}}$ is equal to the association time $t_a = 1/g$ so comparing Eqs. (31) and (30) one may conclude that

$$W^{\text{enc}}(K) \approx 1/[1 + (\lambda|K|)^2] .$$  \hfill (32)

The equality here may be achieved only for asymptoti-
cally small $|K| \rightarrow 0$ in the region of validity of the phe-
nomenological theory. In the Mössbauer experiment, on
the other hand, $|K|$ is finite and comparatively large so
$W^{\text{enc}}$ in Eq. (32) cannot be found in the small-$K$ limit. However, below we will see that the number of impurity jumps $z_{\text{enc}}$ depends only on the small momenta, Eq. (32) should be sufficient for establishing an exact relation between $z_{\text{enc}}$ and $\lambda$.

The relationship can be found with the use of the expression

$$z_{\text{enc}} = \frac{1}{f} \sum_1^N W^{\text{enc}}_1 \frac{1^2}{\epsilon^2}$$  \hfill (33)

which is a slightly rearranged Eq. (8) from Ref. \(^{23}\) written in our notation. In the thermodynamic limit $N \rightarrow \infty$ $W^{\text{enc}}_1$ can be found from the continuum inverse Fourier transform as

$$W^{\text{enc}}_1 = \frac{1}{(2\pi)^3} \iint_{-\pi}^{\pi} dK W^{\text{enc}}(K) e^{-i\vec{K}}$$  \hfill (34)
where dimensionless momentum $\vec{K} = a\vec{k}/2$ was introduced to simplify notation and the use has been made of the cubic symmetry. Substituting this into Eq. (33) and using the identity

$$\delta(\vec{K}) = \frac{1}{(2\pi)^3} \sum_{l} e^{-i\vec{k}\cdot\vec{K}}$$

(35)

it can be seen that $z_{enc}$ depends only on the behavior of $W_{enc}(\vec{K})$ at small $|\vec{K}|$. Indeed, the sum over $l$ in Eq. (33) is calculated by first applying the Laplacian $-\nabla^2 K$ to Eq. (33) and then carrying out the integration over $\vec{K}$ by parts twice. The second derivatives at $\vec{K} = 0$ are calculated with the use of Eq. (32) to give

$$z_{enc} \simeq \frac{12\lambda^2}{f_\infty a^2}$$

(36)

where we replaced general $f$ by $f_\infty$ from Eq. (37) because the phenomenological approach was developed for the case of strong I-v binding. Now substituting $\lambda$ from Eq. (34) into Eq. (36) and using the definition of $D_m$ Eq. (35) one finds

$$z_{enc} = \frac{w_2}{r} = \frac{w_2}{7w_3p_\infty}$$

(37)

where use has been made of the definition of $r$ Eq. (36). As will be discussed below, this expression does not agree with the qualitative conclusions about the dependence of $z_{enc}$ on the 5FM frequencies reached in Ref. 16 on the basis of the MC simulations. The comparison may be not warranted because Eq. (37) has been derived for the strong-coupling case while simulations covered also other cases.

To clarify this issue let us calculate $z_{enc}$ for the general 5FM within the approach of Ref. 24. In this approach the mean number of the impurity jumps is calculated as

$$z_{enc} = 1/(1 - p_R)$$

(38)

where $p_R$ is the probability for the vacancy to return from the first CS on the impurity site. $p_R$ can be found as follows. The rate of the vacancy return on the impurity site is equal to the rate of I-v exchanges $w_2$ irrespective of the binding. The rate of the definite departure of the vacancy away from the impurity is equal to the product of the total rate of the vacancy jumps from the first CS to higher shells $7w_3$ multiplied by the probability to diffuse infinity far from the impurity $p_\infty$. Each factor in the product $r = 7w_3p_\infty(w_4/w_0)$ can also be calculated for any values of the frequencies, not only for the strong binding case. With all rates being known, the return probability is found as the ratio of the return rate to the total rate

$$p_R = \frac{w_2}{w_2 + r}.$$ 

(39)

Substituting this into Eq. (38) one finds

$$z_{enc} = 1 + \frac{w_2}{w_2 + r} = 1 + \frac{w_2}{7w_3p_\infty}.$$ 

(40)

This expression differs from Eq. (37) only on a numerical constant equal to unity while the dependence on the frequencies is the same. It is interesting to note that being derived in a more general case Eq. (40) looks as more reliable than Eq. (37) restricted to the case of tight binding. However, the latter seems to be more physical because when $w_2$ (hence, $pr$) vanish it predicts the correct number of impurity jumps equal to zero while Eq. (40) predicts one jump. Nevertheless, below we will use $z_{enc}$ from Eq. (40) for consistency with Ref. 16.

From Fig. 3 it is seen that $z_{enc}$ from Eq. (40) agrees with the MC simulations for all sets of the 5FM parameters studied in Ref. 16. But the qualitative description of the frequency dependence of $z_{enc}$ suggested in the paper does not agree with Eq. (40). First disagreement concerns the conclusion that $z_{enc}$ strongly depends on $w_1/w_3$ ratio and weakly depends on the ratio $w_4/w_0$. But Eq. (57) does not depend on $w_1$ at all while through $p_\infty$ it strongly depends on $w_4/w_0$ ratio, especially when it is large, as was shown with the use of MC simulations in I and will be further confirmed below within the rigorous solution. Second, when $w_4/w_0 \rightarrow \infty p_\infty \propto w_0/w_4$ and so $z_{enc}$ in Eq. (57) will also strongly depend on the $w_4/w_3$ ratio while in Ref. 16 it was concluded that $z_{enc}$ does not depend on it. One source of the discrepancies seems to be due to the fact that the case of large $w_4/w_0$ ratios was not investigated in Ref. 16 while in our study it was of major importance because the first-principles calculations discussed in I predict that it dominates strong I-v binding, at least in the aluminum host.

Another apparent disagreement concerns roughly Gaussian diffusion profiles obtained in the MC simulations in Ref. 16 despite the large I-v attraction which...
according to our findings might lead to NGDPs. This, however, is explainable by the small value of the parameter $\lambda = 0.4a$ that can be calculated with the use of Eqs. (30) and (37) on the basis of the experimentally fitted frequencies and $z_{\text{enc}} \approx 2.46$. The small values of both quantities are mainly due to the small value of $w_2$ found in the fit. Thus even in the case of strong binding the mobility of impurity can be low because of the reduced frequency of the I-v exchanges that define the diffusion. $\lambda$ characterizes the extent of the exponential part of the NGDP. But with $\lambda = 0.4a$ being smaller than even the NN distance non-Gaussian behavior is hardly detectable in the 3D case, though in 2D the microscopic profiles were reliably measured in Refs. 14 and 15. The small value of $z_{\text{enc}}$ and $\lambda$ in the FeAl system were partly due to the high experimental temperature of 923 K. There is not enough data to decide whether NGDPs can be observed in this system at lower temperature, though $\lambda$ usually grows when the temperature is lowered 14,31.

V. DIFFUSION ALONG A SYMMETRY AXIS

A major goal of the present study is to give a rigorous justification to the phenomenological theory of impurity diffusion in the FCC host developed in I. The theory has been based on the notion of the mobile intermediate state of the impurity introduced in Ref. 4 which in the case of the 5FM has been identified in I with the tightly bound I-v pairs. This has made possible derivation of simple formulas for the impurity GF and the diffusion profiles in stark contrast with the complicated expression for the rigorous solution of Sec. III. So our aim in this section is to show that the phenomenological expressions do agree with the rigorous approach in the limits of strong I-v binding and the macroscopic diffusion that corresponds to small values of $z$ and $|\mathbf{K}|$ in the frequency-momentum space or, equivalently, to macroscopic spatiotemporal scale.

In cubic crystals diffusion is isotropic in the limit of small $|\mathbf{K}|$ so instead of a general momentum $\mathbf{K}$ that requires solution of 54 equations, the momentum along a symmetry axis can be chosen in order to reduce the system size. To this end let us chose the direction along $Z$ axis with $\mathbf{K} = (0, 0, K)$. In this case the components of vector $\mathbf{\tilde{p}}_K$ in Eq. (23) can be divided into 13 equivalence classes, as shown in Fig. 1 All components within a class are equal so it is sufficient to retain only one equation for each class which reduces the system of 54 equations to a system of 13 equations

$$ (I - HU)\mathbf{\tilde{p}}_K = P\mathbf{\tilde{c}}_0, $$

where on the r.h.s. only 13 components of vector Eq. (24) corresponding to different classes has been kept, $I$ is the identity matrix of size 13 and $H$ and $U$ are $13 \times 14$ and $14 \times 13$ matrices, respectively, that are obtained from $P$ and $V$ as follows. Because all vector components belonging to one class are the same, their precise coordinates are irrelevant and can be characterized only by the class number which is used as the subscripts of matrices $H$ and $U$. To find $H_{ij}$ one can take any site $n$ from class $i$ and then sum $P_{n-n'}$ over all $n'$ from class $j$. For example,

$$ H_{51} = P_{011} + P_{013} + 2P_{112}, $$

as can be seen from Fig. 1 by taking the leftmost site from class 5 and checking that there is exactly one NN site at $n = (1, 1, 0)$ belonging to class 1 (the leftmost in the figure from this class), one at $n = (3, 0, 1)$ (the rightmost in the class) and two sites at $n = (2, \pm 1, 1)$. It is to be noted that matrices $H$ and $U$ are not symmetric. Besides, one would need also the matrix elements $H_{00}$, where 0 refers to the “class” consisting of the site at the impurity position. $H_{00}$ are necessary to fill the 0-th column of $13 \times 14$ matrix $H$. All expressions of the matrix elements of $H$ in terms of $P_{ij,k}$ needed in calculations below can be found in ancillary file in Ref. 32.

Matrix $U$ can be obtained from $V$ in a similar way by summing all contributions $V_{n,n'}$ into matrix elements between the classes:
where

\[ U_{11} = -2\bar{w}_1 - w_2 - 7\bar{w}_3 - \bar{w}_5 \quad (44) \]
\[ U_{22} = -4\bar{w}_1 - 7\bar{w}_3 - w_5. \quad (45) \]

Matrix \( U \) has the familiar gain-loss structure (see Appendix A) with the barred frequencies \( \bar{w}_i \) in the off-diagonal matrix elements having plus sign and the diagonal terms with the minus sign, but not necessary positive or negative values because of the subtraction of \( w_0 \). Thus, for example, \( U_{41} \) is equal to \( 4\bar{w}_3 \) because there is exactly four sites that are NN to a site in 4th class from which a vacancy may jump at this site with the rates different from \( w_0 \) and similarly \( U_{44} \) is equal to \( -4\bar{w}_4 \) because there is four sites (all from class 1) where the vacancy can jump from a site in class 4 (see Fig. 1).

Because our goal is to find the impurity GF, we are interested only in those components of vector \( \vec{\rho}_{K=(0,0,K)} \equiv \tilde{\rho}_K \) that enter into Eq. (11), that is, only in the components belonging to the first and the third classes. Moreover, because for any NN vector \( \mathbf{e}^{(1)} \) from the first class there exists an NN vector in the third class such that

\[ \mathbf{e}^{(3)} = -\mathbf{e}^{(1)}, \quad (46) \]

it is easily seen that one can express the solution for \( G(K, z) \) in terms of only one of the components because the FCC lattice is centrosymmetric. Because the initial value Eq. (10) was also assumed to be centrosymmetric, the kinetics will preserve the symmetry, so during the whole system evolution the following equality will hold

\[ \langle \mathbf{n} \cdot \mathbf{\dot{v}}_{-1-n} \rangle = \langle \mathbf{n} \cdot \mathbf{\dot{v}}_{1+n} \rangle. \quad (47) \]

Applying the LF-transform Eq. (7) to this equation and changing the summation on the r.h.s. from \( \mathbf{K} \) to \(-\mathbf{K}\) one arrives at the equality

\[ \rho(\mathbf{K}, z, -\mathbf{n}) = \rho(-\mathbf{K}, z, \mathbf{n}). \quad (48) \]

Thus, in view of Eq. (45), only two functions \( \rho_{\pm K}(z, \mathbf{e}^{(k)}) \) with \( k \) being either 1 or 3 are needed for the calculation of the impurity GF in Eq. (11). Choosing \( k = 1 \) with the use of the Cramer’s rule one gets

\[ \rho(K, z, \mathbf{e}^{(1)}) = \Delta_1(K, z)/\Delta(K, z), \quad (49) \]

where

\[ \Delta(K, z) = \det(I - HU) \quad (50) \]

is the determinant of the system in Eq. (41) and \( \Delta_1(K, z) \) is this determinant with the first column replaced by the r.h.s. vector \( \vec{\rho}_0 \) Eq. (74) according to the Cramer’s rule. Due to the axial symmetry Eq. (13) simplifies to

\[ \Sigma(K, z) = -w_2d^2 \sum_{\{\text{upper}\}} \sum_{\{\text{lower}\}} (1 - e^{\pm i\mathbf{a}K/2}) z\rho(\pm K, z, \mathbf{e}^{(1)}), \quad (51) \]

where the summation is over the upper and the lower signs in the summand and \( \mathbf{e}^{(1)} \) is any of the four lattice vectors from the first class. Eq. (51) together with Eq. (14) solves the problem of finding the impurity GF in the uniaxial geometry.

VI. DIFFUSION OF TIGHTLY BOUND I-V PAIRS

In the axisymmetric case the impurity GF is fully determined by the diffusion kernel \( \Sigma \) Eq. (51) which in the limit \( K \to 0 \) in FCC lattice can also describe macroscopic diffusion for any \( \mathbf{K} \) with small absolute value.

In the phenomenological theory only the macroscopic diffusion can be treated. The corresponding diffusion kernel can be found from Eqs. (44) and (53) in I as

\[ \Sigma^{(ph)}(K, z) = -\frac{12\epsilon_{NN} z + g}{z + r + D_m K^2} D_m K^2, \quad (52) \]
where $K^2$ was replaced by $K^2$ to facilitate comparison with the above rigorous expression. Thus, in order to prove equivalence of the phenomenological approach and the rigorous theory in the diffusion limit in the case of strong I-v binding it is necessary to show that Eq. (52) approximately reproduces Eq. (51) at small values of $z$, $K$, and $w_3/w_4$ (see Eq. (53)).

To this end let us first compare the values of the diffusion constant in both approaches. Using Eq. (14) it is easy to show that the diffusion constant is obtained from the diffusion kernel as

$$D = \lim_{z \to 0, K \to 0} \Sigma(K, z)/K^2 = \lim_{z \to 0, K \to 0} D(K, z).$$

Applying this to Eq. (52) one gets

$$D_\infty = gD_m/r,$$  

where the diffusion constant was supplied by the subscript $\infty$ to remind that the phenomenological expression is valid only in the case of strong I-v binding. Eq. (54) is satisfied in the phenomenological theory (see Eq. (55) in 1) and we are going to show that this is also the case in the rigorous approach. This amounts to showing that $D_\infty$ agrees with the known expressions for $D$ in the tight-binding limit. But this would also hold if $D$ is correct for all values of frequencies, not only in the limiting case. Though rigorous analytic expression for $D$ in the canonical version of the 5FM has been derived in Ref. 33, below we present its numerical calculation which has an advantage of admitting generalization to the extended versions of the model. 3,11,20,21

A. The diffusion constant

Correlation effects are conventionally accounted for in the diffusion constant through the correlation factor $f$ defined as 1,26,34

$$D = c_v w_2^2 w_3 \frac{w_4}{w_3} f a^2,$$  

where $f$ in the 5FM case was shown to have the general form 20,33,34

$$f = \frac{2w_1 + 7F(w_4/w_0)w_3}{2w_1 + 2w_2 + 7F(w_4/w_0)w_3}. $$

This expression has been thoroughly studied in literature and so may serve as a stringent test for new calculation techniques.

The limit $K \to 0$ in Eq. (53) can be calculated by first expanding the $K$-dependent quantities in the nominator and denominator of Eq. (51) to the second order in $K$ as

$$D(0, z) = w_2^2 a^2 \rho(0, z, e^{(1)}) + 4w_2^2 a^2 \frac{d \rho(0, z, e^{(1)})}{dK} \bigg|_{K=0}. $$

In this notation

$$D = \lim_{z \to 0} D(0, z).$$

The limit is straightforward to calculate for the first term on the r.h.s. of Eq. (57). As is easily seen from the definition of the LF transform Eq. (7), if the correlation function Eq. (11) has a non-zero asymptotic when $t \to \infty$, the Laplace part of the transform develops the singularity $\sim \frac{1}{z}$. But at large times and in the absence of macroscopic fluxes, which is the case when $K = 0$, all kinetics die out and the correlation function tends to its equilibrium value

$$\langle \hat{n}_v n_{v+n} \rangle_{t \to \infty} \to N^{-1} \langle \hat{n}_v n_{v} \rangle^{(eq)} = N^{-1} c_{n}^{(eq)},$$

where $c_{n}^{(eq)}$ is the equilibrium vacancy concentration at site $n$ relative to the impurity; the factor $1/N$ appears due to the fact that as $t \to \infty$ the only impurity in the system occupies any of $N$ sites with equal probability $1/N$. The LF transform Eq. (7) of Eq. (59) at $K = 0$ gives

$$\lim_{z \to 0} z \rho(0, z, n) = c_{n}^{(eq)}.$$  

Thus, the first term on the r.h.s. of Eq. (57) in the limit $z \to 0$ is equal to

$$w_2 a^2 c_{n}^{(eq)} = w_2 a^2 c_v w_4/w_3$$

where use have been made of Eqs. (11) and (12).

The limit $z \to 0$ in the last term of Eq. (57) concerns only $\rho$ so it is convenient to first obtain it with the use of Eq. (24)

$$\lim_{z \to 0} z P\bar{c}_0 = c_v$$

and (49) as

$$\lim_{z \to 0} z \rho(K, z, e^{(1)}) = c_v \bar{\Delta}_1(K, 0)/\Delta(K, 0),$$

where $\bar{\Delta}_1$ differs from $\Delta_1$ in that instead of $P\bar{c}_0$ the limiting value Eq. (62) is substituted and, besides, the vacancy concentration is factored out of the determinant so that the first column of $\Delta(K, 0)$ should be replaced simply by the column of unitaries. Further, using the reflection symmetry of the 1D geometry it can be shown that determinant $\Delta(K, 0)$ is an even function of $K$, so only $\Delta_1$ contributes to the derivative in Eq. (57). The dependence of $\bar{\Delta}_1$ on $K$ comes only from the matrix element

$$U_{13} = w_2 \exp(iaK/2)$$

of matrix Eq. (13) that contributes to the third column of matrix $I - HU$ the terms of the form:

$$\delta(I - HU)_{j3} = -w_2 H_{j3} \exp(iaK/2).$$

Similar contributions to column one from the matrix element $U_{31}$ disappear from $\Delta_1$ because this column is replaced by unitaries. Thus, differentiation of $\bar{\Delta}_1$ with respect to $K$ in the limit $K \to 0$ amounts to the following
expression for the second term in the diffusion constant Eq. (67)

\[ 4w_2i0 \frac{d[z\rho(K, z, e^{1(1)})]}{dK} \bigg|_{z,K=0} = 2c_2w_2a^2 \frac{\Delta_{13}}{\Delta} \bigg|_{z,K=0}, \]

where \( \Delta_{13} \) is the determinant of matrix \( I - HU \) where the first column is replaced with unities and the third one with the terms \( w_2H_{11} \). Now adding the two terms in Eq. (67) in the limit \( z \to 0 \) with the use of Eqs. (60), (D2), and (D6) and using the definition of the correlation factor Eq. (55) one arrives at

\[ f = 1 + 2\frac{w_3}{w_4} \frac{\Delta_{13}}{\Delta} \bigg|_{z,K=0}. \] (67)

To compare with \( f \) in Eq. (56) the latter was solved with respect to \( F \) as

\[ F\left( \frac{w_3}{w_4} \right) = 2\frac{w_2}{w_3} \left( 1 - f - w_1 \right) \] (68)

and \( f \) from Eq. (67) was calculated for more than \( 10^5 \) randomly generated quartets of the ratios \( 10^{-5} < w_i/w_0 < 10^5 \), \( i = 1 - 4 \). The calculated values were substituted in Eq. (68) and as can be seen from Fig. 4 where for brevity only about 10% of the simulation data are presented, no noticeable dependence on \( w_i/w_0 \), \( i = 1 - 3 \) is discernible. This supports the results of Refs. 33 and 34 and confirms the assumption that the general form of \( f \) in Eq. (56) is exact to the leading order in \( c_\rho \).

B. Diffusion kernel in the strong-binding limit

The expression for \( D \) obtained from Eqs. (53) and (D4) is valid for all values of the frequencies, including the tight-binding case. Thus, Eq. (53) provides one relation between three phenomenological parameters and the known diffusion constant so in order to calculate all of them in the rigorous approach two additional relations are needed. Let us begin with the calculation of the decay rate \( r \). It does not enter as a parameter in the rigorous solution but has to be found from the assumption that in the tight-binding case the exact diffusion kernel has the form of Eq. (52) and that \( r \) depends only on \( w_3 \) and \( w_4/w_0 \) as in the phenomenological expression Eq. (D6). Confirmation of these assumptions in the framework of the rigorous theory would provide a nontrivial check of the phenomenological approach.

As is seen from Eq. (122), strong I-v binding means either small value of \( w_3 \), or large value of \( w_4 \), or both. The difficulty in studying the tight-binding limit within the rigorous approach is that the cases \( w_3 \to 0 \) and \( w_4 \to \infty \) should be studied separately because the frequencies enter in a different manner in both the decay rate Eq. (D6) and in the determinants that define the diffusion kernel, as can be seen from Eqs. (13), (49), (41), and (13). Therefore, let us start from the \( w_3 \to 0 \) case. We first note that the determinants in Eq. (52) are polynomial in their matrix elements so the singular behavior at \( z, r, K \to 0 \) may originate only from the determinant in the denominator of Eq. (49) which in this limit should be representable as

\[ \Delta = \Psi(z, K, w_3)(z + \xi + \bar{D}_mK^2), \] (69)

where \( \xi \) and \( \bar{D}_m \) are underlined to indicate that in this expressions they in general are functions of \( z \) and \( K \). When the latter variables are equal to zero the underlined quantities would coincide with the constants \( r \) and \( D_m \). The function \( \Psi \) is fixed by the condition that \( z \) in the second factor has the coefficient equal to unity when \( z, K, w_3 \) are equal to zero and \( \Psi(0, 0, 0) \neq 0 \); for brevity, only the variables that change their values in the expressions below are explicitly shown as the arguments of \( \Psi \) with other parameters being treated as constants.

From Eq. (69) one can derive the derivatives of the determinant over its arguments as

\[ \partial \Delta/\partial z \bigg|_{z,w_3,K=0} = \Psi(0, 0, 0), \] (70)

(Additionally assuming that \( \xi \propto w_3 \)) so that if the decay rate has the form of Eq. (D6) then

\[ p_\infty = \frac{1}{7} \left. \frac{\partial \Delta/\partial w_3}{\partial \Delta/\partial z} \right|_{z,K,w_3=0}. \] (71)

should be the function of only the ratio \( w_4/w_0 \) and should agree with the runaway probability defined in I. In Fig. 4 it can be seen that this is indeed the case.

Similarly,

\[ D_m = \left. \frac{\partial \Delta/\partial K^2}{\partial \Delta/\partial z} \right|_{z,K,w_3=0}. \] (72)
calculated for $\sim 10^5$ randomly generated frequency ratios agreed with Eq. (D5) to within the accuracy of the calculations. With the use of Eq. (51) and taking into account that $D, D_m, $ and $r$ in the tight-binding case have the same values as in the phenomenological theory to the accuracy of the numerical calculations, we conclude that the value of the association rate $g$ in the rigorous approach also has the correct value.

To finalize comparison with the phenomenological theory in the $w_3 \to 0$ case it remained to consider the contribution due to the associated pairs that may be present in the initial state. The contribution is given by the term in Eq. (52) proportional to $CN_N$

$$\delta\Sigma^{(ph)} = -\frac{12c_{NN}z}{z + r + D_mK^2}D_mK^2.$$  \hspace{1cm} (73)

In Eq. (51) this term should originate from Eq. (49) through the similar contribution in the initial condition Eq. (24)

$$\delta(P\delta_{i0})_n = 12c_{NN}P_n.$$  \hspace{1cm} (74)

In the Cramer’s rule solution it can be separated from the rest of the terms because determinants are linear functions of the column vectors. Explicit expression for $\delta\Sigma$ can be derived from Eqs. (51) and (49) with $\Delta_1$ in the last equation replaced by $\Delta_\rho$, where $\vec{P}$ is the vector of size 13 composed of $P_n$ from Eq. (74) with $n$ belonging to the respective classes (all $P_n$ within the class are the same). Now taking into account representation Eq. (69) for $\Delta$, $\delta\Sigma$ from Eq. (51) can be cast in the form similar to Eq. (73) as

$$\delta\Sigma \approx -\theta(z, K, w_3)\frac{12c_{NN}z}{z + r + D_mK^2}D_mK^2$$  \hspace{1cm} (75)

where notation is the same as in Eq. (69) and in $\theta(z, K, w_3)$ are gathered all factors not present in the rest of the equality. Next, from Eq. (73) it is easy to see that

$$-\lim_{K \to 0} \left[ \delta\Sigma^{(ph)}/(12c_{NN}z) \right]_{z, r = 0} = 1.$$  \hspace{1cm} (76)

Similar transformation of Eq. (75) leads to the following condition of the agreement between the rigorous approach and the phenomenological theory:

$$\theta(z \to 0, K \to 0, w_3 \to 0) \to 1.$$  \hspace{1cm} (77)

The limit $K \to 0$ in the expression for $\delta\Sigma$ in terms of the determinant ratio can be found similar to the case of the diffusion constant in Sec. VI A. But a simpler route is to calculate it numerically. For $K = 0.01$ $10^5$ trios of the ratios $w_1/w_0, w_2/w_0,$ and $w_3/w_0$ has been generated and Eq. (77) has been found to be satisfied with very high accuracy.

In the second case of tight-binding $w_4/w_0 \to \infty$ all calculations were performed along the above lines with a few technical modifications. From the computational point of view the main difference between the two cases is that the determinants in Eq. (19) are polynomials of tenth order in $w_4$, as can be seen from Eqs. (69) and (50) so when $w_4 \to \infty$ their ratio may be hard to compute with sufficient precision. The difficulty was resolved by dividing the last ten columns in the determinants by $w_4$ so both the matrix elements and the determinants became bounded as $w_4 \to \infty$ and thus easily manageable numerically. The condition $w_3 = 0$ in the equations above was replaced by the condition $1/w_4 = 0$ and the derivative over $w_3$ replaced by the derivative with respect to $1/w_4$. The calculations performed with the use of this trick confirmed asymptotic equivalence of the rigorous solution to the phenomenological theory also in this case.

**VII. I-V INTERACTION OF ARBITRARY STRENGTH**

The phenomenological theory developed in I has been based on the notion of the mobile impurity state which in the case of the 5FM has been identified with the tightly bound I-v pairs. In previous sections we succeeded in showing that the expressions derived in I can be rigorously justified within the rigorous approach but only in the limit of tight binding. But this regime is obviously not universal and in different systems I-v interaction will exhibit either only a weak or no attraction or the repulsion. The rigorous solution in principle covers all possible cases but in view of the physical transparency and simplicity of the phenomenological theory it would be desirable to be able to assess its applicability in the cases when the tight-binding condition is not obviously satisfied. Besides, the pair diffusion picture predicts such interesting and unusual phenomena as the NGDPs and the non-Fickian diffusion but as was noted in the Introduction, in Refs. 9, 10, and 13 it was shown that NGDPs can occur even in the absence of I-v attraction. This poses the question of whether the phenomenological theory does not miss possible additional contributions into the NGDP phenomenon. This question should also be addressed within the rigorous approach.

Unfortunately, the rigorous solution is difficult to deal with because of its complexity. Even in the simpler uniaxial case it has been expressed through complex $13 \times 13$ determinants which apparently can be calculated only numerically. Besides, to find the diffusion profiles the solution has to be inversely LF-transformed back to the space-time variables which is a nontrivial task even in the simple 1D geometry. Explicit expression for the transformed impurity GF reads:

$$G_i(t) = \frac{1}{2\pi i} \int dz e^{zt} \frac{1}{L} \sum_{K} e^{iaKl/2}G(K, z),$$  \hspace{1cm} (78)

where $L$ is the number of planes along the chosen (100) direction. The contour in the integration over $z$ in Eq. (78) is defined as the vertical line passing to the right of
all singularities of the integrand.\textsuperscript{35,36} But it can be shown that in the 5FM all perturbations relax to the equilibrium state corresponding to the zero-eigenvalue eigenmode and all other eigenvalues are negative real numbers.\textsuperscript{27,28} Therefore, the integration contour can be deformed as shown in Fig. 5. Now using the Green’s functions property
\begin{equation}
G(K, z^*) = G^*(K, z) \tag{79}
\end{equation}
(the star means complex conjugate) we can restrict the integration only to one of the contour branches as
\begin{equation}
\frac{1}{2\pi i} \int dz e^{izt}(K, z) = \frac{1}{\pi} \text{Im} \int_{\gamma C^-} dz e^{izt}G(K, z) \rightarrow \frac{1}{\pi} \int_{-\infty}^{0} dE e^{Et} \text{Im} G(K, E^-), \tag{80}
\end{equation}
where in the limit \( \varepsilon \rightarrow 0 \) the integration is over the negative real axis with \( E = \text{Re}z \) and \( E^- = E - i\varepsilon \).

Thus, to calculate the diffusion profile at time \( t \) one has to first integrate the imaginary part over \( E \) for every Fourier momentum \( K \) and subsequently recover \( G(X = al/2, t) \) via the inverse Fourier transform. Even for small diffusion length of \( \sim 10 \text{ nm} \) in aluminum where \( a/2 \approx 0.2 \text{ nm} \) one will have to cover the spatial range \( \sim 100 \text{ nm} \) \( \sim 500 \) lattice planes in \( \{100\} \) direction which gives an order of magnitude estimate of the number of \( K \)-points (hence, integrations over \( E \)) needed in the calculation. Farther, in performing the integrations over \( E \) one has to calculate at every mesh point the complex-valued functions \( P_{\alpha}(z) \) from Eq. (17) that enter into the determinants via matrix \( H \) and vector \( P_{\alpha}0 \) which can also be calculated only numerically. And the mesh in \( E \) should be sufficiently fine because, as we will see below, \( \text{Im}G(K, E^-) \) may vary rather steeply. The problem somewhat alleviates in the diffusion limit \( t \gg 1/w_0 \) when the exponential function in Eq. (80) dumps the integrand at large negative values of \( E \) so the integration range in the vicinity of \( E = 0 \) can be chosen to be of \( O(1/t) \approx w_0 \). The number of \( P_{\alpha}(z) \) that need be calculated in the general case is sixteen (see Ref. \textsuperscript{32}) though they can be recursively calculated in terms of only three of them which, in their turn, can be expressed through the complete elliptic integrals.\textsuperscript{37-39}

\section*{A. Dissociation of NN I-v pairs}

Though the bound pairs dominate the diffusion only at sufficiently strong I-v attraction, the diffusion in the 5FM always goes via exchanges within NN I-v pairs. So the difference with the binding case is only in the availability of the vacancy strongly enhanced in the case of tight binding. This may amount to larger number of I-v exchanges \( z_{enc} \) and to longer mean diffusion distance \( \lambda \) during one encounter which could translate in enhanced diffusion constant and macroscopic NGDP. However, the example of the FeAl\textsubscript{1-x} system shows that this is not always the case. Because of the small value of the exchange frequency \( w_2 \) both \( z_{enc} \approx 2 \) and \( \lambda \approx 0.4a \) remain small despite the small decay rate \( r \) in the denominator of Eq. (10).\textsuperscript{34} Thus, a question arises on whether there exists a possibility to detect strong I-v attraction in similar cases. Below with the use of the rigorous solution we are going to show that though the transition between the cases of strong binding and its absence is not abrupt, there exists a qualitative differences between the time evolution of the bound and non-bound I-v pairs with intermediate cases exhibiting mixed behavior.

To see this, let us first consider the phenomenological theory where the diffusion of the bound pair can be described by the LF-transformed pair GF
\begin{equation}
G_{ph}^p(K, z) = \frac{1}{z + r + DmK^2} \tag{81}
\end{equation}
that in the continuum space satisfies the initial condition
\begin{equation}
G_{ph}^p(R, t = 0) = \delta(R) \tag{82}
\end{equation}
(see Eqs. (35) and (37) in I). As follows from the Fourier transform definition and from Eq. (81), the time evolution of the total density of bound pairs can be found from the inverse Laplace transform of the GF at \( K = 0 \) as
\begin{equation}
G_{ph}^l(t) = \frac{1}{\pi} \int_{-\infty}^{0} dE \text{Im} G_{ph}^p(0, E^-) e^{Et} = e^{-rt}, \tag{83}
\end{equation}
where the last equality was obtained with the use of the identity
\begin{equation}
\text{Im} G_{ph}^p(K, z = E - i\varepsilon)|_{\varepsilon \rightarrow 0} = \pi\delta(E + r). \tag{84}
\end{equation}

In the lattice case the definition of the pair GF is not completely straightforward because NN I-v pair cannot be placed on one site but occupies two sites. The point
pair of the phenomenological approach is natural to associate with the smallest pair occupying two NN sites. But because there are 12 such sites around the impurity on the FCC lattice, the total density of NN pairs should be equal to the sum of 12 densities from Eqs. (4) and/or (9) with \( n = e \). In the \( K = 0 \) case in Eq. (83) all 12 densities are equal so the total pair density

\[
G_p(K = 0, z) = 12\rho(K = 0, z, e)|_{c_0 = 0.12 c_{NN} = 1} \tag{85}
\]

can be calculated with any of the NN vectors \( e \). In this definition the vacancy concentrations in the initial state Eq. (6) were chosen to correspond to only one NN vacancy near the impurity in otherwise empty system. Physically this describes evolution of one associated pair from the initial configuration during time interval when new associations with the bulk vacancies can be neglected (\( c_0 = 0 \)). This may correspond to an early stage of out-of-equilibrium evolution when \( t \ll t_a \) and the number of NN pairs in the initial state is large. The latter can be achieved by means of an appropriate preparation method, such as the ion implantation technique \( ^{27} \) or in the tight-binding as a consequence of the strong I-v attraction when the initial state is prepared in equilibrium at different temperature and free vacancies anneal faster than the bound ones.

The density \( \rho \) on the r.h.s. of Eq. (85) can be found with the use of the solution Eq. (49) as

\[
G_p(K = 0, z) = 12\Delta_2(0, z) / \Delta(0, z)|_{c_0 = 0.12 c_{NN} = 1} \tag{86}
\]

The time evolution of the NN density can be found by substituting \( G_p(K = 0, E^-) \) into Eq. (85) and calculating the integral over \( E \). Unfortunately, in general case the GF can be calculated only numerically. But a qualitative insight can be obtained from the analytic expression for the 4FM GF (see Appendix [E]) which will be used below in the discussion of the 5FM.

From Eq. (21) with the vacancy concentrations as in Eq. (86) and \( n = e \) with the use of Eqs. (118) and (123) one arrives at the expression

\[
G_{4FM}^p(K = 0, z) = \frac{1}{z + 1} \tag{87}
\]

that formally coincides with its phenomenological homologue Eq. (31) except that now the decay rate is not a constant but a function

\[
\tau(w_3, z) = \frac{w_3 P_c^{-1}(z) - z(z + 13)}{z + 12} \tag{88}
\]

where \( H_{10} \) was replaced by \( P_c^{22} \).

A comment is in order about the dimensionalities in Eq. (88) and in equations below. The expressions needed in derivation of the analytic solution in Appendix [E] are rather cumbersome so it was found convenient to set \( w_0 = 1 \) to simplify them. This can be achieved either by introducing the “natural” time unit \( w_0^{-1} \) or by restoring the missing dimensional coefficients as powers of \( w_0 \) in the final expressions. This should not cause difficulty because all relevant quantities have dimensionality of time or its inverse (the rate or frequency) while the quantities of dimension of length enter only via the dimensionless combination \( K = aK/2 \).

Eq. (88) connects \( P_0(z) \) in Eq. (85) with the extended Watson’s integral \( P_0(z) \) which analytic properties are well known (see Ref. [39] and references therein). The most important to us is that \( P_0(z) \), hence, \( P_0(z) \) have the square root singularities at \( z = 0 \) (in 3D lattices to which the discussion below will be restricted) which engenders important consequences. Namely, because for \( E < 0 \) \( \sqrt{E} \) is imaginary, the imaginary part of GF in Eq. (87) extends over all negative values of \( E \), as can be seen in Fig. 6 and is not concentrated at a single point as in the phenomenological approach. Due to the exponential term in the integrand the \( t \rightarrow \infty \) asymptotic of the integral in Eq. (86) is dominated by the small values of \( |E| \), so the asymptotic will be of the power-law type \( \sim t^{-1/2} \), not exponential as in the phenomenological theory. Moreover, because for small absolute values of \( z \) \( |z| \ll \sqrt{|z|} \), a priorly it is the square-root contribution that should be kept in approximations for GF at small \( |z| \) while \( O(z) \) terms should be neglected. But \( z \) in the denominator of \( G_p^{(ph)} \) originates from the time derivative of the phenomenological diffusion equation (see Eq. (34)) in I and similar equations in Refs. [34] and [35], so by neglecting it the possibility to describe the I-v pairs as diffusing quasiparticles is lost.
These observations are fully confirmed by the curves in the lower panel of Fig. 6 which cannot be approximated by the sharp delta-function imaginary part of the phenomenological GF in Eq. (84) even crudely. In the upper panel, however, the tallest curve is strongly peaked and its approximation by a delta-function seems reasonable. The difference between the two cases is in the structure of the denominator in Eq. (77). At small $|E|$ the GF can be approximated to three leading powers of $E$ as

$$G_p(K = 0, E < 0) \approx \frac{1}{E + r(1 - iC_r \sqrt{|E|})},$$

(89)

where $C_r$ is a positive real constant of order unity. We dropped the 4FM superscript because in Sec. VI B the validity of Eq. (89) was, in fact, proved in the general 5FM case, though only by numerical means. The key feature of Eq. (89) is that as $r \to 0$, the square root term enters into GF only with the prefactor $r$, similar to the exact 4FM expression Eq. (88). If it were not so in the 5FM case, the partial derivative over $z$ in Eq. (70) would have been infinite at $z, r = 0$ so $p_\infty$ and $D_m$ in Eqs. (71) and Eq. (72) would be equal to zero, which was not seen neither in $w_3 = 0$ case, nor for $w_4 = \infty$. The importance of the prefactor $r$ is that it makes possible for the phenomenological theory to hold for the values of $E$ satisfying the inequalities

$$C_r r \sqrt{|E|} \ll |E| \ll 1$$

(90)

which can be satisfied for sufficiently small $r$. Thus, according to Eq. (89) the pole singularity which in the phenomenological theory is positioned at the real $z$ axis at $E = -r$ in the rigorous theory is shifted to the complex plane on the distance $\propto r^{3/2} \ll r$ from the real axis, so as $r \to 0$ the width of the peaked structure in the imaginary part of GF shrinks to zero and acquires delta-function-like shape. It will dominate the integrand at not too large values of the time variable $t$ and the NN pair density will behave as $\propto e^{-rt}$, thus justifying the phenomenological approach for tightly bound pairs.

However, at small but finite values of $r$ the exponential factor in the integrand sooner or later will suppress the quasiparticle contribution, so at very large times the singularity at $E = 0$ will still determine the $t \to \infty$ asymptotic behavior. This is illustrated in Fig. 7 where the integrand of Eq. (83) is shown at several stages of the evolution.

As is seen, at some stage the integrand becomes dominant and the quasiparticle behavior ceases to define the physics of the pair dissociation. This can be used for establishing the range of validity of the phenomenological theory by estimating the time interval during which the quasiparticle picture remains adequate for a given value of the decay rate $r$. It seems reasonable to assume that the peaked structure dominance ends when the value at the local maximum of the integrand near $E = -r$ becomes equal to the maximum near $E = 0$. The value of the latter is found by standard means from the approximate expression

$$\text{Im} \ G_p(K = 0, E^{-} e^{Et})_{E \to 0} \approx C_r \sqrt{|E|} e^{Et}/r.$$  

(91)

Up to $O(1)$ factors it scales at small $r$ and large $t$ as $\sim 1/(r\sqrt{t})$. Near the peak at $E = -r$ the integrand behaves as $\sim e^{-rt}/r^{3/2}$ so the crossover time between the two regimes scales as

$$t_c \sim -\ln r/r.$$  

(92)

Thus, for $t < t_c$ the phenomenological description should be valid while for larger times the power-law behavior should be observed. In more physical terms this time interval can be estimated from the exponential decay law in Eq. (83) that describes the evolution of the density of bound pairs. Taking the initial density as unity, at time $t_c$ according to Eqs. (82) and (83) it will decrease to $r$. In Table II I several systems with strong I-v binding were identified on the basis of available first-principles data.\textsuperscript{11,12} The parameter $w_0/w_4$ which is proportional to $r$ when $w_4$ is large varied in those systems in the range $\sim 10^{-4} - 10^{-7}$ which suggests that the exponential decay may remain valid in the pair density range in several orders of magnitude from unity to $10^{-4} - 10^{-7}$. But there exists a natural time limit for the pair decay to be observable. It is defined by the association rate $g$ which defines the average association time $t_a$ Eq. (25). When $t_a$ is comparable to $t_c$, the new pairs in the tight-binding case will associate before the endpoint singularity contribution becomes detectable, so experimentally only the exponential behavior may be seen.

In the opposite case when the decay rate is of order unity the square root behavior in the integrand of Eq.
Experimental observation of the decay could be helpful in experimental and theoretical validation of the 5FM. The usefulness of the model is hampered by the large number of parameters in its definition which cannot be measured experimentally. In Ref. 41 on the basis of EM it was argued that in cubic lattices only two of the five frequencies can be found. This can be seen from the phenomenological solution Eq. (D3) in which the diffusion kernel is fully characterized by only two parameters \( \lambda \) and \( g \). As we saw in Sec. LV the encounter approximation corresponds to setting \( z = 0 \) in the diffusion kernel while keeping its full momentum dependence. In contrast, in the pair GF which is closely related to the diffusion kernel (cf. Eqs. (S3) and (11)) we have set the momentum to zero but retained \( z \)-dependence intact, so it may be expected that this would provide supplementary information to that obtainable from the momentum dependence. Indeed, if measured, the time evolution of the density of the tightly bound pairs would make possible determination of the decay rate \( r \) which cannot be obtained from the parameters \( g \) and \( \lambda \). Specifically, in Ref. 41 it has been shown that \( w_2 \) and \( w_3 \) cannot be uniquely defined from the experimental data because they are linearly correlated and the same data can be described by different frequency sets. The authors discussed FeCu\textsuperscript{22} system with a weak I-v attraction which is difficult to analyze because of the complexity of the general diffusion kernel. But in the strong binding case \( r \) in Eq. (17b) depends on \( w_3 \) but do not depend on \( w_2 \) so the knowledge of \( r \) will impose a restriction on \( w_3 \) that is independent of \( w_2 \).

In Ref. 41 it was suggested that information about internals of I-v pairs can be obtained from the measurement of the impurity hyperfine interactions. Another prospective approach for the experimental study of the NN pairs may provide the positron annihilation technique (see Ref. 42 and references therein). In most cases the electron density inside a vacancy depends on whether the vacancy is associated with an impurity or is surrounded only by the host atoms. As a consequence, the lifetime and/or the momentum distribution of the gamma radiation produced by the annihilation of the positron caught within the vacancy will depend on whether the vacancy is associated or not. The contribution of the associated vacancies can be separated from the annihilation spectra and its time evolution may provide direct information about the decay of NN pairs.

VIII. CONCLUSION

In the present paper a rigorous solution of the 5FM for the FCC lattice has been obtained. Formally the solution is exact only to the first order in the vacancy concentration but because of the small vacancy concentration in solids this accuracy most probably exceeds the accuracy of the model itself; besides, in order to account for higher order corrections that may be necessary in some cases the 5FM should first be extended to include additional many-body interactions that contribute to higher orders of the expansion.\textsuperscript{16} So from a physical standpoint the first-order solution is the best one that can be obtained within the framework of the conventional 5FM.\textsuperscript{2,3}

The model solvability is a consequence of the fact that 5FM describes interactions between only two particles: the impurity and the vacancy and two-body problems can usually be solved exactly. The method of solution developed in Secs. II and III is quite general and can be straightforwardly generalized on other lattices and on more sophisticated models like those suggested in literature for more realistic description of the diffusion. The generalizations proposed on the basis of physical arguments and the first principles calculations\textsuperscript{3,11,20,21} usually include the vacancy jumps to higher CSs and longer-ranged I-v interactions. However, in Ref. 41 it was pointed out that this would necessitate introduction of additional phenomenological parameters while even the parameters of the conventional 5FM cannot be fully determined from experimental data. The results of the present paper may somewhat alleviate this difficulty. The high accuracy of the solution should make the fit of the additional parameters more reliable than within less rigorous approaches. Besides, in Sec. VII A it has been shown that the time dependence of dissociation of the NN I-v pair density can provide an additional constraint on the parameters so it would be desirable to develop techniques for its experimental measurement. It has been suggested that in addition to the hyperfine interactions technique suggested in literature the positron annihilation is another prospective method for the study of associated I-v pairs. Besides, such experiments will make possible investigation of the tight binding in the cases when the binding energy is large but for some reason the mean pair diffusion distance \( \lambda \) is small. FeAl system is one such case where \( \lambda \) is small because of the small value of the I-v exchange frequency.\textsuperscript{19} A number of similar systems can be predicted on the basis of the first-principles calculations\textsuperscript{11,12} as, e. g., SA\textsubscript{1} where \( E_0 = 0.46 \) eV but \( \lambda \) is only about 1 nm at the room temperature.

The method of solution developed in the present paper is applicable only to the models with finite-range interactions. In this case the infinite set of REs can be reduced to a finite system of linear equations and solved by the Cramer’s rule. But because the equations are linear, a rigorous solution in the case of long-range interactions that appear, e. g., in some problems of dopant diffusion in semiconductors\textsuperscript{20} should be also feasible.
A major goal of the present study was to rigorously justify the phenomenological approach developed in I on the basis of the mobile state concept of Ref. [4] that was introduced for the description of dopant diffusion in silicon. By assuming that the mobile state in the 5FM coincides with the tightly bound I-v pairs, a complete agreement between the phenomenological expression for the impurity GF in I and the tight-binding limit of the rigorous solution has been established. Thus, the possibility of observation of the most interesting phenomena such as the NGDPs [15] and the non-Fickian diffusion in the FCC systems with the vacancy mediated diffusion has been rigorously substantiated.

But the rigorous solution can be also used when the conditions of validity of the phenomenological approach are not fulfilled. The approach is applicable only to the macroscopic diffusion at large spatiotemporal scale and only in the case of strong I-v attraction. These conditions are not satisfied, for example, in such techniques as the quasielastic neutron scattering, the coherent X-rays, and the Mössbauer spectroscopy where experimental data on the impurity diffusion are gathered at large Fourier momenta that in the real space correspond to microscopic distances [12,16,25]. As has been shown in Sec. IV the diffusional broadening of the Mössbauer resonance in FeAl obtained in the framework of the rigorous approach accords well both with experimental data and with theoretical calculations within the EM [16,22,25]. Besides, it has been possible to establish quantitative relations between the parameters of the phenomenological theory and of the EM which may be helpful in cross-checking the data obtained within the two approaches.

Further, in view of the ongoing advancement of experimental techniques toward the microscopic scale, an important advantage of the rigorous solution is that it describes the impurity density at the lattice sites, i.e., at the atomic level. Thus, in addition to the macroscopic diffusion describable also within the phenomenological theory the rigorous approach is able to describe the microscopic diffusion. From the results of Refs. 9, 10, 14, and 15 it may be concluded that the microscopic NGDPs should exist in practically all host-impurity systems, including those with I-v repulsion. So the phenomenon should be ubiquitous and the rigorous approach provides adequate means for its theoretical description for any values of the 5FM parameters.

But there exist important differences between the behavior of the NN pairs in the presence of strong binding and its absence. In Sec. VII it has been shown that the NN pairs decay follows the exponential law in the tight-binding case and the power law otherwise. More important difference concerns the non-Fickian diffusion predicted in the phenomenological theory 14,13,31,43. It originates from the fact that in bound I-v pair the vacancy mediating the diffusion is permanently available, so the diffusion flux due to the bound pairs is unrelated to the distribution of the surrounding impurities and can be non-zero in their absence (see, e.g., the discussion in I) or even be directed along the concentration gradient (uphill diffusion 43). Also, the diffusion equation for the pair diffusion does not agree with the second Fick’s law because the pairs are unstable and this their flux (hence, the flux of the impurities they contain) is not conserved [43]. But this self-sustained diffusion can persist only during the pair lifetime and so is restricted to distances of order $\lambda$. Fick’s laws describe impurity diffusion at the macroscopic scale, so they are hardly applicable to the microscopic diffusion where $\lambda$ is of order of the lattice constant or smaller. So the non-Fickian diffusion should be sought in the systems with tightly bound pairs and macroscopic values of $\lambda$.

In I it was shown that large $\lambda$ at the room temperature may be found in about 20% of impurities in the aluminum host studied in the first-principles calculations in Refs. 11 and 12. Unfortunately, at present the 5FM parameters obtained in such calculations are not reliable enough to predict even the sign of the I-v interaction in some cases. For example, in FeAl system the calculations predict I-v repulsion [12] while experimentally the interaction is attractive and quite strong [16]. Nevertheless, it is believed that while not reliable in concrete cases, the first-principles calculations can describe general trends in large classes of systems [15]. From this standpoint it can be expected on the basis of the aluminum database [12] that I-v attraction should exist in about half of the systems, though in many cases rather weak. But in stochastic dynamics the strength of the interaction is measured with respect to the temperature, so it may be hoped that at sufficiently low temperatures there exist FCC impurity-host systems with the vacancy-mediated diffusion that exhibit the phenomena characteristic of the non-Fickian diffusion similar to those observed in the impurity diffusion in semiconductors 4,13,31,43.

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Appendix A: Master equation

The master equation (ME) [47] describes time evolution of the set (or vector) of probabilities $\langle p_M(t) \rangle$, where $M$ denotes possible states of the system, for a stochastic system to be found in state $M$ at time $t$. Eq. (A1) is a set of liner equations with a gain-loss structure in which the probability for the system to be found in state $M$ grows due to transitions from other states $M'$ with the rates $W_{MM'}$ (the first term on the r.h.s.) and diminishes when the system leaves state $M$.
For some other state given by the negative second term. More compactly ME can be written as
\[ \frac{dp_M(t)}{dt} = \sum_L \tilde{W}_{ML} p_L(t), \tag{A2} \]
where
\[ \tilde{W}_{ML} = W_{M \neq L} - \left( \sum_{M' \neq M} W_{M'M} \right) \delta_{ML}. \tag{A3} \]

The inequality signs here can be dropped if we agree that \( W_{MM} = 0 \) for all \( M \). This is legitimate because Eq. (A1) does not depend on the diagonal elements of \( W \). From Eq. (A3) it is easy to see that
\[ \sum_M \tilde{W}_{ML} = 0 \tag{A4} \]
which means that the total probability \( \sum_M p_M \) is conserved by ME, as follows from Eq. (A2).

The ME is an efficient tool for studying systems with a small number of states, like the I-v pair that consists only in a few average quantities. As is seen, new average value appeared on the r.h.s. to \( \delta_0 \) to obtain a finite closed system of REs some approximations would be necessary. In the main text of the article this was achieved by restricting consideration by the linear terms in the vacancy concentration. In Appendix B below a concrete example of application of the ME will be presented.

**Appendix B: Vacancy diffusion in perfect crystal**

The problem of a vacancy diffusing in a periodic lattice is a simple example of application of the ME. Let us denote the probability for the vacancy to be found on site \( n \) at time \( t \) as \( p_n(t) \) and assume that initially the vacancy occupies site \( 0 \)
\[ p_n(t = 0) = \delta_{n0}. \tag{B1} \]

The vacancy jumps between NN sites with the same rate \( w_0 \) so the matrix in Eq. (A3) is
\[ \tilde{W}_{nm}^0 = w_0 \left( \sum_e \delta_{n+e,m} - 12 \delta_{nn,m} \right), \tag{B2} \]
where \( e \) is the set of 12 vectors that connect NN sites on the FCC lattice. Substituting Eq. (B2) into Eq. (A1) one gets
\[ \frac{dp_n(t)}{dt} = \sum_m \tilde{W}_{nm}^0 p_m(t) = w_0 \left( \sum_e p_{n+e}(t) - 12 p_n(t) \right). \tag{B3} \]

Because the equation has constant coefficients, it can be solved with the use of the LF transform Eq. (7). Applying it to Eq. (B3) and solving the resulting algebraic equation one arrives at the solution
\[ P(K, z) = \frac{1}{z + w_0 a^2 \epsilon_K}, \tag{B4} \]
where
\[ \epsilon_K = a^{-2} \sum_e \left[ 1 - \exp(i a K \cdot e/2) \right] \tag{B5} \]
is defined in such a way that at small \( |K| \) \( \epsilon_K \approx K^2 \), so that the coefficient before \( \epsilon_K \) in Eq. (B4) can be identified with the vacancy diffusion constant
\[ D_v = w_0 a^2. \tag{B6} \]

In Sec. III we need expressions for the inverse Fourier transform of \( P(K, z) \)
\[ P_n(z) = \frac{1}{N} \sum_K \frac{\exp[-iaK \cdot n/2]}{z + a^2 w_0 \epsilon_K}, \tag{B7} \]
which are the well-known lattice GF and Watson’s integrals. In Refs. 57 59 sophisticated analytical relations between \( P_n(z) \) and the complete elliptic integrals were derived that make possible efficient techniques of their calculation at arbitrary complex values of \( z \). For \( z = 0 \) that is sufficient in the majority of calculations in the present paper accurate values of all necessary \( P_n(z) \) can be found by direct numerical integration of Eq. (B7) with the use of the Monkhorst-Pack method.24
From Eq. (B3) a useful relation between \( P_n(z) \) can be derived
\[
(z + 12w_0)P_n = \delta_{0n} + w_0 \sum_{e} P_{n+e} \tag{B8}
\]
which can be used to express \( P_n \) with a large value of \(|n|\) through \( P_m \) with \(|m| < |n|\). Efficiency of this technique is enhanced by the fact that \( P_n \) satisfy all symmetries of the cubic point group so that all \( P_n \) with any permutations of the components of vector \( n \) with any signs are equal.

Appendix C: Dyson’s equation

From the standpoint of the Mori-Zwanzig memory-function approach the impurity GF studied in the main text is, up to normalization, the impurity autocorrelation function and so can be treated within this formalism. The Dyson equation for the autocorrelation function that we are interested in is derived as follows. First one needs to re-write ME Eq. (A1) in the vector-matrix notation as
\[
\frac{d}{dt}|t\rangle = \hat{W}|t\rangle \tag{C1}
\]
where vector \(|t\rangle\) has as its components the probabilities \( p_M(t) \) and \( \hat{W} \) is now the evolution operator acting on the vector. The probability normalization \( \sum_M p_M(t) = 1 \) in the vector notation can be expressed as the scalar product
\[
(1|t\rangle = 1, \tag{C2}
\]
where the components of vector \((1| \) are equal to unity for all \( M \), so the product is just the sum over all states. Eq. (C1) can be formally solved as
\[
|t\rangle = e^{\hat{W}t}|t = 0\rangle, \tag{C3}
\]
where we assumed that \(|t = 0\rangle\) is the initial state of the system and operator \( \hat{W} \) is time-independent.

To proceed farther we introduce two equal size sets of the “bra”
\[
\langle \tilde{b}| = \langle 1| \tilde{1} \tag{C4}
\]
and of the “ket” vectors
\[
|b_{nm}\rangle = \delta_{mn}|0\rangle, \tag{C5}
\]
where \( \delta_{mn} = 0, 1 \) is the impurity occupation number on site \( n \). The scalar product of the vectors
\[
\langle \tilde{b}_l|b_{mn}\rangle = \langle 1|\tilde{1}b_{nm}|0\rangle = N^{-1} \delta_{lm} \tag{C6}
\]
is found as follows. The Kronecker symbol appears because there is only one impurity in the system, so different sites cannot be occupied simultaneously; \( \langle 1|\tilde{1}|0\rangle \) is the probability of finding the impurity at site \( 1 \) which is equal to \( 1/N \) because all sites are equivalent.

Following the standard procedure one introduces the projection operators \( \mathcal{P} \) and \( \mathcal{Q} \) defined as
\[
\mathcal{P} = N \sum_{n} |b_{n}\rangle \langle \tilde{b}_n| = 1 - \mathcal{Q}, \tag{C7}
\]
which satisfy the usual conditions \( \mathcal{P}^2 = \mathcal{P} \), etc. Besides, as is easy to see,
\[
\mathcal{Q} |b_{n}\rangle = 0 \tag{C8}
\]
for any \( n \).

The correlation function
\[
C_{lm}(t) = \langle \tilde{b}_l|e^{\hat{W}t}|b_{mn}\rangle \tag{C9}
\]
describes the probability of finding the impurity at site \( m \) in the initial state and at site \( l \) at later time \( t \). As is seen, this definition differs from the definition of GF in only one point: in the probability of finding the impurity in the initial state which is equal to \( 1/N \). In the definition of GF this probability is defined as the certainty, i.e., the impurity is at site \( m \) with probability one. Thus,
\[
G_{lm}(t) = NC_{lm}(t). \tag{C10}
\]

The Laplace transforms of the correlation function Eq. (C9) can be formally calculated as
\[
C_{lm}(z) = \int_{0}^{\infty} dt e^{-zt}C_{lm}(t) = \langle \tilde{b}_l| \frac{1}{z-\hat{W}}|b_{mn}\rangle. \tag{C11}
\]
Now with the use of Eq. (C8) and the operator identities \( 1 = \mathcal{P} + \mathcal{Q} \) and
\[
\frac{1}{x-y} = \frac{1}{x} + \frac{1}{x-y} \tag{C12}
\]
Eq. (C11) can be transformed as
\[
C_{lm}(z) = \langle \tilde{b}_l| \left( \frac{1}{z} + \frac{1}{z-\hat{W}} \hat{W} \mathcal{P} \frac{1}{z-\hat{W}} \right) |b_{mn}\rangle. \tag{C13}
\]
Using Eq. (C7) one finds
\[
\mathcal{P} \frac{1}{z-\hat{W}} |b_{mn}\rangle = N \sum_{n} |b_{n}\rangle \langle \tilde{b}_n| \frac{1}{z-\hat{W}} |b_{mn}\rangle \tag{C14}
\]
Substituting this into Eq. (C13) and using Eqs. (C6), (C10), and (C11) one gets
\[
G_{lm}(z) = \frac{\delta_{lm}}{z} + N \langle \tilde{b}_l| \frac{1}{z-\hat{W}} \hat{W} |b_{mn}\rangle G_{nm}(z). \tag{C15}
\]
This is an alternative form of the Dyson equation in lattice coordinates. To see this we first apply the identity Eq. (C12) to Eq. (C14) to get
\[
G(K,z) = \frac{1}{z - \Sigma(K,z)} = \frac{1}{z} + \frac{1}{z} \Sigma(K,z) G(K,z). \tag{C16}
\]
This would coincide with the Fourier transformed Eq. (C17) provided the self-energy is

$$\Sigma(\mathbf{K}, z) = \sum_i e^{-i\mathbf{K} \cdot \mathbf{r}_i} N(b_i) \frac{z}{z - W_Q} \bar{W} \langle b_0 \rangle$$ (C17)

where the choice \( n = 0 \) has been made to simplify the expression and \( \mathbf{K} = \alpha \mathbf{K}/2 \). Eq. (C17) is rather complicated because it is exact to all orders in \( c_q \). But as was argued in the main text, only the first order term is physically sound and it can be obtained by simpler means.

**Appendix D: Expressions from the phenomenological theory**

Below are listed some formulas that are needed for comparison with the phenomenological approach in the main text. Their derivation can be found in I.

In the phenomenological theory the strong I-v attraction is characterized by large binding energy \( E_b > 0 \) which defines the equilibrium density of the vacancies on the impurity NN sites as

$$\langle \rho_{eq} \rangle = c_v e^{E_b/k_B T}$$ (D1)

and enters the detailed balance condition that imposes the restriction on the jump frequencies:\( ^{20,30,34} \)

$$\frac{w_3}{w_4} \approx \exp \left( -\frac{E_b}{k_B T} \right) \to 0.$$ (D2)

In the phenomenological theory the diffusion kernel at \( z = 0 \) is

$$\Sigma^{(ph)}(\mathbf{K}, 0) \approx -g \left( 1 - \frac{1}{1 + (\lambda \mathbf{K})^2} \right)$$ (D3)

(see Eq. (69) in I). The mean pair diffusion distance is

$$\lambda = \sqrt{D_m/r}$$ (D4)

(Eq. (27) in I), where the pair diffusion constant

$$D_m = \frac{w_2(w_1 + w_3)a^2}{12(w_1 + w_2 + w_3)} = \frac{w_2}{12} f_\infty a^2$$ (D5)

and the pair decay rate

$$r = 7w_3 p_\infty(w_4/w_0)$$ (D6)

were introduced in I in Eqs. (24) and (28);

$$f_\infty = \frac{w_1 + w_3}{w_1 + w_2 + w_3}$$ (D7)

is the correlation factor \( f \) in the strong coupling limit (Eq. (7) in I); \( p_\infty \) is the probability of the vacancy in the I-v pair to diffuse from the impurity NN site at the spatial infinity.

**Appendix E: The four frequency model (4FM)**

In the calculations of the diffusion constant for the 5FM it has been noted\(^ {20,33} \) that the matrices needed in the derivation greatly simplify when \( w_4 = w_0 \). It turns out that in the general case of the diffusion kernel the matrices in the determinants in the Cramer’s solution Eqs. (47), (50), and (51) also become much simpler in this case. When \( w_4 = w_0 \) the nonzero matrix elements remain only in the first three columns of matrix \( U \) in Eq. (45) and as a consequence in the matrix product \( HU \). The physical reason for this is clear. As can be seen from Fig. 1 the region of influence of the impurity shrinks in this case to only the first CS which in the axisymmetric case contains only three components of vector \( \bar{\rho} \) on the r.h.s. of Eq. (18), so the set of equations, hence, the size of determinants in Eq. (49) can be reduced to three:

$$\Delta|_{w_4 = w_0} \equiv \begin{vmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{vmatrix} = \begin{vmatrix} 1 + 4H_{10} - H_{11} + 2(H_{11} - H_{12})\bar{w}_1 + (H_{11} - H_{13}e^{-i\mathbf{K}})w_2 + Aw_{\bar{w}} \\ 4H_{10} - H_{21} + 2(H_{21} - H_{22})\bar{w}_1 + (H_{21} - H_{23}e^{-i\mathbf{K}})w_2 + B\bar{w}_3 \\ 4H_{10} - H_{13} + 2(H_{13} - H_{23})\bar{w}_1 + (H_{13} - H_{11}e^{-i\mathbf{K}})w_2 + C\bar{w}_3 \end{vmatrix} \begin{vmatrix} d_{12} = d_{21}(\mathbf{K} = 0) \\ d_{13} = d_{31}(\mathbf{K} = 0) \end{vmatrix} \begin{vmatrix} d_{21}^{\mathbf{K}} \\ d_{31}^{\mathbf{K}} \end{vmatrix}.$$ (E1)

where the vertical lines on both sides of a matrix denote its determinant and the superscripts designate the change of sign \( K \to -K \).

Additional simplification takes place in determinant \( \Delta_1 \) in the numerator of the Cramer’s solution Eq. (49) due to the fact that in \( 3 \times 3 \) determinant only three components of the r.h.s. vector \( \bar{\rho}_e = P_{011} \) corresponding to NN sites are needed. But all these components are equal because they depend on the same function \( P_e = P_{011} \) so that similar to Eq. (53) the determinant can be calcu-
lated with the first column in $\Delta$ replaced by unities

$$\Delta_1 = \Delta|_{A_1=1, i=1-3} \quad (E2)$$

and then multiplied by the factor

$$\eta_{NN} = (\bar{P}_0 c_v) = \frac{c_v}{z} + [(c_{NN} - c_v)(12 + \frac{z}{w_0}) - c_v]P_{011}.$$ \hspace{1cm} (E3)

Further details of the calculation of determinants $\Delta$ and $\Delta_1$ are given in Sec. E1 below. Substituting Eqs. (E10) and (E23) into Eqs. (19) and (11) one gets

$$G(K, z) = \frac{1}{z} \left( 1 - \frac{8w_2\eta_{NN}A_1A_2(1 - \cos K)}{A_1(A_2 + 2C_2w_2)A_3 + 2w_2[A_3(C_2(A_4 + 2H_1z_1) + C_4w_3) - A_2C_3A_4(1 - \cos K)]} \right). \quad (E4)$$

where

$$f|_{w_3=0} = \frac{A_2}{A_2 + 2C_2w_2} = \frac{w_1}{w_1 + w_2}. \quad (E8)$$

Now substituting the approximate expressions Eqs. (E6) into Eq. (E7) and remembering that $K = aK/2$ one finally gets

$$G(K, z) \approx \frac{1}{z} \left( 1 - \frac{(12\eta_{NN}/C_3)D_m^{w_3=0}K^2}{z^2 + w_3/C_3 + D_m^{w_3=0}K^2} \right). \quad (E9)$$

where $D_m$ is given by Eq. (E5) and $\eta_{NN}$ by Eq. (E5). Eq. (E9) will agree with Eq. (52) from I provided that, first,

$$w_3/C_3|_{z=0} = r = 7w_3p_\infty(w_4/w_0) = 1. \quad (E10)$$

This is indeed the case because of the following chain of equalities

$$C_3^{-1}|_{z=0} = (12P_{011})^{-1}|_{z=0} = 2.90 = 7p_\infty(1), \quad (E11)$$

where the last equality was obtained in MC simulations in I. The contributions proportional to $C_{NN}$ and $\eta_{NN}$ in Eq. (52) in I also fully agree with the 4FM expression Eq. (E9), as can be shown with the use of Eqs. (E3), (E11) and Eq. (57) from I

$$g = 84c_vw_4p_\infty, \quad (E12)$$

where in the 4FM $w_4$ should be replaced by $w_0$.

Thus, in the case of 4FM the phenomenological limit of the impurity GF can be rigorously obtained by analytic means.

1. Calculation of determinants

The coefficients of $\bar{w}_3$ in Eq. (E11) are the following combinations of the matrix elements $H_{ij}$:

- $A = 7H_{11} - 4H_{14} - H_{15} - 2H_{17} - H_{18} - H_{1,11}$
- $B = 7H_{21} - 2H_{15} - H_{18} - H_{19} - H_{1,12}$
- $C = 7H_{31} - H_{15} - 4H_{16} - H_{19} - 2H_{1,10} - H_{1,13}$
- $E = 7H_{22} - 2H_{25} - H_{28} - H_{29} - H_{2,12}, \quad (E13)$
Though the determinant of a $3 \times 3$ matrix can be calculated analytically with the use of known elementary formula, in the case of Eq. (E15) the resulting expressions will be still too awkward for analysis. In this Appendix several tricks are suggested to simplify the task. The main tool to use is the identity Eq. (B8) satisfied by functions $P_ijk(z)$. In Refs. [77–79] it was shown that $P_ijk(z)$ with any indexes can be expressed through only three of them. In our calculations we used this possibility only partially by reducing $H_{ij}$ in Eqs. (E13) with high indexes to lower ones as

\begin{align*}
A &= 1 + 4H_{10} - (z + 3)H_{11} + 2H_{12} \\
B &= 4H_{10} - (z + 3)H_{12} + 2H_{22} \\
C &= 4H_{10} - (z + 3)H_{13} + 2H_{12} \\
E &= 1 + 4H_{10} - (z + 5)H_{22} + 4H_{12} \quad \text{(E14)}
\end{align*}

\[\Delta = \begin{vmatrix}
    zH_{11} + 2(H_{11} - H_{12})w_1 + (H_{11} - H_{13}e^{-ik})w_2 + Aw_3 & d_{12} = d_{21}(K = 0) & d_{13}^{(-K)} \\
    zH_{12} + 2(H_{12} - H_{22})w_1 + H_{22}(1 - e^{-ik})w_2 + Bw_3 & zH_{22} + 4(H_{22} - H_{12})w_1 + Ew_3 & d_{23}^{(-K)} \\
    zH_{13} + 2(H_{13} - H_{12})w_1 + (H_{13} - H_{11}e^{-ik})w_2 + Cw_3 & d_{12} & d_{13}^{(-K)}
\end{vmatrix}, \quad \text{(E15)}\]

First let us consider the simpler case of the determinant $\Delta_1$ that is obtained from $\Delta$ by placing unities in the first column in Eq. (E15). By subtracting the first line from the second and the third ones a triangular matrix is obtained with determinant

\[\Delta_1 = (d_{22} - d_{12})(d_{13}^{(-K)} - d_{31}^{(-K)}). \quad \text{(E16)}\]

Using explicit expressions for $d_{ij}$ from Eqs. (E14) and (E15) it is easy to transform Eq. (E16) to

\[\Delta_1 = A_1[A_2 + C_2w_2(1 + e^{iK})], \quad \text{(E17)}\]

where

\begin{align*}
A_1 &= d_{22} - d_{12} = w_3 + C_1[z + 6w_1 - (z + 7)w_3] \\
C_1 &= H_{22} - H_{12} \\
A_2 &= w_3 + C_2[z + 2w_1 - (z + 3)w_3] \\
C_2 &= H_{11} - H_{13}
\end{align*}

The calculation of $\Delta$ is more complicated but it can be simplified by the observation that at $K = 0$ all columns sum to the same value

\[A_3 = C_3z + [1 - z(z + 13)H_{10}]w_3 \quad \text{(E18)}\]

where

\[C_3 = (z + 12)H_{10}. \quad \text{(E19)}\]

This can be shown with the use of the identities of the kind

\[H_{11} + H_{12} + H_{13} = 2H_{12} + H_{22} = C_3, \quad \text{(E20)}\]

Similarly, by replacing barred frequencies $\bar{w}_k$ in Eq. (E11) with $w_k - 1$ (we remind that $w_0$ was set to be unity) it is possible to cast the determinant in the form

\[A + B + C = 2B + E = 1 - z(z + 13)H_{10}, \quad \text{(E21)}\]

etc., obtained with the use of Eq. (B8). At finite $K$, by adding the first and the third rows to the middle one the second row will contain the following matrix elements:

\[A_3 + C_3w_2(1 - e^{-iK}), A_3, A_3 + C_3w_2(1 - e^{iK}) \quad \text{(E22)}\]

With $A_3$ given by Eq. (E18) it is seen that in the limit of strong binding $w_3 \to 0$ and the diffusion limit $z, K^2 \to 0$ all terms in the row are small being of the first order in all these quantities. Because $\Delta$ can be calculated as the sum of these terms multiplied by corresponding minors,

\[\Delta = A_1(A_2 + 2C_2w_2)A_3 + 2w_2(A_3C_2(A_4 + 2H_{12}w_1) + C_4w_3) - A_2C_3A_4(1 - \cos K), \quad \text{(E23)}\]

where

\begin{align*}
A_4 &= zH_{12} - 2C_1w_1 + Bw_3 \\
C_4 &= H_{13} - 2C_2(2H_{10} + H_{12}) \quad \text{(E24)}
\end{align*}

this shows that the general form of the determinant Eq. (E9) can be rigorously justified at least in the 4FM.

The derivations above are rather cumbersome but their validity can be checked numerically. Because all identities used are purely algebraical, they can be verified for real values of both $z$ and $iK$ (i.e., for complex $K$). As was pointed out in Sec. B for $z \geq 0$ all $P_{ijk}$ can be efficiently computed with the use of the special points technique. All identities verified in this way were found to be correct in most cases almost to the accuracy of the double precision arithmetic for all values of $z$ and $K$ studied.
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