Trapping of point defects in alloys

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Based on the random walk of point defects in alloys, neglecting the interaction between the components and their interaction with the point defects, the kinetics of the annihilation of point defects in fcc alloys is studied by computer simulations. Particularly, the dependence of the mean trapping time in random alloys on various parameters, including the structure of traps, the composition of alloy, and the mobility ratio of the components, is investigated and reported here.

I. INTRODUCTION

The problem of trapping of point defects (PD's) has been studied mostly by the theory of continuous diffusion.[1] However, the application of the theory of the random walk (RW) of PD's (Refs. 2–4) yields another approach to this problem. By using the simple symmetric RW model, various problems concerning the behavior of PD's in crystals, such as the number of distinct sites visited by a PD during an N-step jump and the probability of a PD returning to its origin or the mean time needed by a PD for reaching a certain lattice site, have been already treated analytically. However, the analytical treatments using the RW method contain one of two simplifications.

(1) an idealized random walk is assumed, in which all neighbor sites of the PD executing a RW possess the same probability of being occupied by the next migration step of the PD. This idealization, which implies the indistinguishability of all lattice sites, is generally denoted as *symmetric* RW. It may be realistic in a lattice composed of a single type of atoms. In alloys the *nonsymmetric* RW generally takes place.

(2) An idealized trapping process is assumed in which the reaction zone of the trap is supposed to consist only of a single lattice site (reaction radius=0). The PD is considered to be irreversibly trapped immediately after having reached the lattice site in the reaction zone of the trap. This idealization is denoted here as *ideal trapping*. In reality, however, the structure of a trap and its interaction with the PD is much more complicated and the *nonideal trapping* occurs.

Based on the RW approach, in the present paper Monte-Carlo simulations (MCS's) will be applied to the trapping problem in fcc alloys. By maintaining the simplifications with the irreversibility of the PD-trap reaction and the lack of long-range interaction the problem of the nonsymmetric RW in alloys will be dealt with. Moreover, the nonideal trapping is introduced by taking various trap structures into consideration. In this way the dependence of the trapping time on the different parameters, such as the composition of alloy and the mobility ratio of the components, can be studied. Finally the results from the simulations will be compared with those of the traditional treatments by using the theory of continuous diffusion in which problems including nonsymmetric RW and nonideal trapping have been extensively investigated.[1,5,6]

II. THE FUNDAMENTALS UNDERLYING THE SIMULATIONS

In this work the trapping of the PD's is considered to be determined only by diffusion, and the reaction between traps and PD's is assumed to take place irreversibly and infinitely rapidly, as in conventional treatment by the RW approach[3,4] and by diffusion model.[5,6] Based on these suppositions the trapping kinetics is simplified as the problem of how an arbitrarily migrating PD meets with a trap randomly distributed in the lattice.[5,6]

In the following mainly two quantities will be of interest: (i) the probability they are not trapped after N jumps, which is defined as escape probability V_N and (ii) the average time $\tau_{\rm tr}$ for trapping of the migrating PD. Let p_N denote the probability of being trapped at the Nth step, the trapping time is given by

$$\tau_{\rm tr}=\langle N_{\rm tr}\rangle\bar{\mu}^{-1}\ , \tag{2.1}$$

where

$$\langle N_{\rm tr}\rangle=\sum_{N=1}^{\infty}Np_N \tag{2.2}$$

corresponds to the statistical average of the jump number before trapping and $\bar{\mu}$ is the jump frequency of the PD. For the escape probability we get

$$V_N=1-\sum_{k=1}^{N}p_K\ . \tag{2.3}$$

It follows in addition to Eq. (2.2)

$$\langle N_{\rm tr}\rangle=\sum_{N=1}^{\infty}[V_{N-1}-V_N]N\ . \tag{2.4}$$

Two types of the trapping models have been used for the analytical treatments in case of a symmetric RW and

ideal trapping.

(1) The method suggested by Rosenstock[7] considers the case of an infinite lattice with randomly distributed traps. The probability for a PD to be trapped at the next step is proportional to the probability of meeting a lattice site never visited before. The trapping problem is thus connected with the simple RW. Rosenstock[7] has derived the following approximate expression (see also Appendix A):

$$p_N=\rho_{\mathrm{tr}}(\langle S_N\rangle-\langle S_{N-1}\rangle)(1-\rho_{\mathrm{tr}})^{\langle S_N\rangle-1} . \tag{2.5}$$

Here $\langle S_N\rangle$ denotes the number of the distinct sites visited by a PD during its N jumps and ρ_{tr} the density of the traps. The trapping time can then be calculated

$$\langle N_{\mathrm{tr}}\rangle=\sum_{N=1}^{\infty} N\rho_{\mathrm{tr}}(\langle S_N\rangle-\langle S_{N-1}\rangle)(1-\rho_{\mathrm{tr}})^{\langle S_N\rangle-1} . \tag{2.6}$$

For the small concentration of traps ($\rho_{\mathrm{tr}}<0.05$) the Rosenstock approximation gives further

$$\langle N_{\mathrm{tr}}\rangle=\frac{1-(1-\rho_{\mathrm{tr}})^{1-F}}{\rho_{\mathrm{tr}}(1-F)} \tag{2.7}$$

or for $\rho_{\mathrm{tr}}\ll 1$

$$\langle N_{\mathrm{tr}}\rangle=\frac{1}{(1-F)\rho_{\mathrm{tr}}} . \tag{2.8}$$

F is the probability for the PD to return to its origin, $F=0.3405$ for the simple cubic (sc) lattice, and $F=0.2563$ for the fcc lattice.[8]

(2) The other approach was applied by Montroll[8] by using the periodic boundary condition. It is assumed that the infinite lattice can be divided into periodic sublattices and each of them contains a single trap. The trapping problem is then to observe how the sublattice will be traversed by a PD executing a symmetric RW. After this simplification we have for the trapping time

$$\langle N_{\mathrm{tr}}\rangle=\begin{cases}\frac{1}{\pi}M\ln M+0.195M+o(1) & \text{for square lattice}\\ 1.52M+o(M^{1/2}) & \text{for sc lattice},\end{cases} \tag{2.9}$$

where M is the total number of lattice sites of the periodic sublattice. Since here $1/M$ gives the concentration of traps ρ_{tr}, one recognizes a good agreement between the Eq. (2.9) and (2.8) in the case of a sc lattice.

Both Eqs. (2.8) and (2.9) yield a trapping time independent of the number of jumps N and prove to be a useful approximation for small trap density.[4] The trapping of random walks for higher trap density has been investigated recently in Refs. 9 and 10. In this paper only the density range in which Eqs. (2.8) and (2.9) are valid, as $\rho_{\mathrm{tr}}<10^{-4}$, will be considered.

In the MCS's the critical problems are how to produce an infinite crystal lattice and how to introduce an infinite walk time. For the investigation of $\langle S_N\rangle$ Beeler[11] solved the first problem in his simulations by using the memory of 1000 jump histories. It was assumed that after this large number of jumps the return probability of the PD to its origin can be neglected. By investigating $\langle S_N\rangle$ as a function of the step number N, the limit behavior of $\langle S_N\rangle$ for N going to infinite ($N\rightarrow\infty$) could be determined. On the other hand, by studying the limit behavior of the dependence of $\langle S_N\rangle$ on M for $M\rightarrow\infty$, the second difficulty can also be removed. The results obtained by these treatments were found to be in good agreement with the analytical solution.[3,12] Because of the simple algorithm and the relatively high accuracy, the boundary condition of the periodic sublattice used by Montroll for his analytical treatment will also be used in these simulations.

In the case of symmetric RW all lattice sites are indistinguishable, and thus the jump frequencies of PD's to all neighboring sites are assumed to be equal. But in a real alloy the jump frequency of a PD may strongly depend on the configuration of the neighboring atoms, particularly on the type of atom sitting on the lattice site to which the PD is going to jump. In these simulations, however, it is assumed, for the sake of convenience, that the ordering energy in our A-B computer-generated crystal is small compared to kT, so that the influence of the configuration on the jump frequency of each component can be neglected. Furthermore, the two components A and B can be considered to be distributed randomly. (For simulation the random alloy simplification is not necessary. It is possible to simulate the interaction between the constituents, e.g., by introducing the pair potential, as done for the simulation of tracer diffusion[13] or for the simulation of short range order formation.[14]) Then the jump frequency depends only on the type of atom with which the PD is going to exchange lattice site. Thus for a binary alloy there are two constant jump frequencies μ_A and μ_B.

Concerning the structure of traps for a PD such as a vacancy, they can be formed by all kinds of lattice imperfections. In this simulation for fcc binary alloys the following four different types of traps will be considered: (a) zero-dimensional (0D) traps with a reaction range of a single lattice site [Fig. 1(a)] as they are assumed in the traditional version of the RW theory of trapping with a reaction radius equal to 0 (ideal trapping), (b) 0D traps with a reaction range including only the nearest neighbors (NN's) so that for the fcc lattice this range contains 13 lattice sites [Fig. 1(b)], (c) 0D traps with a reaction range including the next-nearest neighbors (NNN's) so that this range contains 19 lattice sites [Fig. 1(c)], and (d) one-dimensional (1D) traps, which means that the reaction radius of this kind of trap is infinitely large in one dimension and finite in the normal plane. Figure 1(d) shows such a trap in the $\langle 110\rangle$ direction for the fcc lattice with a reaction range including the next-nearest neighbors (NNN's) so that this range contains seven lattice sites per $\langle 110\rangle$ atomic plane. In the simulations only a trap-PD pair, namely, a single trap of one of these kinds and a single PD, is introduced into a (periodic) sublattice. Since then only the relative movement between the arbitrarily distributed trap and the arbitrarily migrating PD is of significance, exactly the same results are ob-

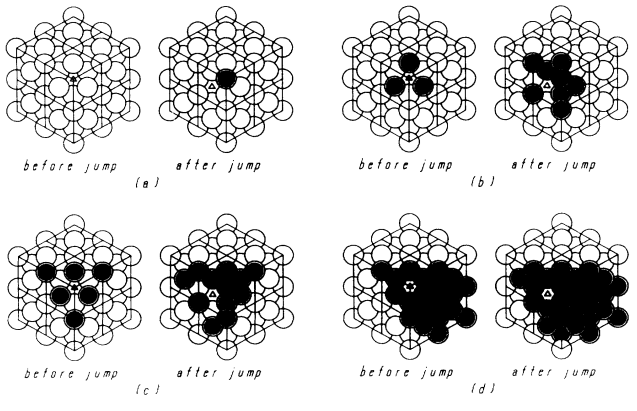

FIG. 1. The structure and the motion of the different kinds of traps. Triangles represent the position of traps. (a) 0D trap with reaction radius=0, 1 lattice site in reaction region; (b) 0D trap with reaction radius to NN, 13 lattice sites in reaction region; (c) 0D trap with reaction radius to NNN, 19 lattice sites in reaction region; (d) 1D trap with reaction radius to NNN, 7 lattice sites per {110} plane in reaction region.

tained by exchanging the role of PD and trap, i.e., by fixing the PD distributed in the lattice at random and letting the trap make a random walk with the mobility and the migration character, which the PD would have had. After this treatment the PD, which arbitrarily situates on a lattice site, has the same probability as a normal lattice site of being visited by the "migrating" trap.

The movement of the different kinds of traps is illustrated in Fig. 1 with the trap being marked with a triangle. All lattice sites that have already been once or more in the reaction region of the moving traps are filled in black.

For a finite crystal of size M in contrast to Eq. (2.5) we have (Appendix A)

$$p_N=\frac{q_N-q_{N-1}}{M} \ . \tag{2.10}$$

Particularly, Eq. (2.3) further yields

$$V_N=1-\frac{q_N}{M} \ , \tag{2.11}$$

where q_N gives the number of the distinct lattice sites visited by the PD or here the migrating trap during N steps of its RW. For $N\to\infty$, $M\to\infty$, q_N is identical with the well-known quantity $\langle S_N\rangle$. Thus Eq. (2.11) indicates that the escape probability V_N is equal to the fraction of the lattice sites in the sublattice never visited during N steps, namely, the fraction of the rest of the white lattice sites in Fig. 1. Equation (2.11) is valid even for traps with very complicated structures. It is thus the aim of the treatment with the mobile trap and fixed PD to achieve a definite expression for the escape probability.

III. PROCEDURE AND RESULTS OF THE SIMULATION

A. Procedure of the simulations

The computer crystal is composed of $45\times45\times45$ fcc elementary cells ($M=364\,500$) for the 0D traps (types a, b, and c). For the 1D trap (type d), $M=150\times150\times16$ and $L=150\times150$ is used for the nonideal trapping as well as $M=600\times600\times1$ and $L=600\times600$ for the ideal trapping. L denotes the size of the (110) lattice plane for the 1D trap lying in the [110] direction. If M_A and M_B denote the number of the lattice sites occupied by A atoms or by B atoms, respectively, $C_X=M_X/M$ ($X=A,B$) gives the composition of the computer alloy. The trap moves into the nearest-neighbor site—exactly in the opposite way as the considered PD would have moved—with a frequency μ_X, if this site is occupied by an X atom. For each attempted jump the jumping direction and thus also the type of the jumping atom is arbitrarily determined among the 12 nearest neighbors. An attempted jump succeeds if the momentary energy fluctuation is large enough to overcome the energy barrier.[15] In this present simulation the jump into the selected X atom is considered to be successful if the random number is smaller than the corresponding normalized jump frequency of the PD $\omega_X=\mu_X/(\mu_A+\mu_B)$.

The main quantity to be calculated by the simulation is the "escape probability" V_x, equal to the fraction of lattice sites never visited by a migrating trap x ($x=a$, b, c, and d) during the time t in which N jumps succeed. Among all these N jumps, N_A comes to site exchanges with A atoms and N_B to those with B atoms, respectively. Since for a homogenous random alloy all sites are statistically indistinguishable, we obtain the relation

$$N_A=C_A\mu_A t \ , \quad N_B=C_B\mu_B t \ . \tag{3.1}$$

In the analysis in this paper, the number of jumps per A atom given by $n_A=N_A/M_A$ will be preferred for the time scale, instead of the real time t or the total jump number N. For the transformation to the real-time scale we have

$$t=\frac{Mn_A}{\mu_A}=\frac{Mn_B}{\mu_B} \tag{3.2}$$

In addition to the dependence on trap structures, the dependence of trapping kinetics on the variables, such as the composition C_A ($C_A=0.25$, 0.5, and 0.75 will be used) and the mobility ratio $\phi=\mu_A/\mu_B$ will be dealt with by the simulation.

In the present simulation the mean trapping time is not directly obtained by investigating the probability that a certain lattice site will be visited after time t but indirectly by studying the behavior of V_x against n_A. In contrast to the direct method, this indirect method is insensitive to the starting point of RW in a finite lattice. By testing runs it was demonstrated that the course of $V_x(n_A)$ is hardly influenced by any variation of the set of random numbers. About the same $V_x(n_A)$ curves have been obtained by making S runs in the small crystal as a single

run in a crystal S times larger. This means that the fluctuation of $V_x(n_A)$ curves follows the usual statistic law, namely, it varies proportionally with $1/\sqrt{\alpha M}$ if α denotes the number of the tests. In order to make the resulting curve more smooth, particularly in the long-time period, various simulation runs have been repeated up to 30–50 times for each given set of parameters C_A and ϕ. The arithmetic average of n_A and V_x are calculated as the functions of the Monte Carlo step and will be used for the evaluation later.

B. Results

Some results of the simulation are plotted in Fig. 2 as $\ln V_x$ vs n_A. The deviation from the inserted solid lines are essentially due to insufficient averaging and less of systematic nature. Corresponding to the different trap structures, the curves have different characters.

(1) The case of the 0D trap with a reaction radius to NN and NNN (types b and c) appears to be the simplest. The corresponding escape probability curves V_b or V_c obviously obey the simple exponential function

$$V_x=\exp\left[-\frac{t}{\tau_x}\right]=\exp\left[-\frac{n_A}{\psi_x}\right]=\exp\left[-\frac{n_B}{\psi'_x}\right] \quad (x=b,c)\,, \tag{3.3}$$

where ψ_x or ψ'_x is the number of jumps per A or B atom during the time τ_x in which V_x reduces to $1/e$. ψ_x and ψ'_x are functions of C_A and ϕ but turn out to be independent of the size of the sublattice M. From Eq. (3.2) we have

$$\tau_x=\frac{\psi_x M}{\mu_A}=\frac{\psi'_x M}{\mu_B}\,. \tag{3.4}$$

According to Eq. (2.4) the trapping time can be derived from

$$\tau_{\rm tr}=-\sum_{t=0}^{\infty} t\Delta V_x=-\int_0^{\infty}\frac{dV_x}{dt}t\,dt \tag{3.5}$$

with $-\Delta V_x=V_x(t)-V_x(t+\Delta t)$ giving the probability of being trapped in the time interval $t\sim t+\Delta t$. By inserting the simulation results $V_x=\exp(-t/\tau_x)$ into this formula it is recognized that the trapping time $\tau_{\rm tr}$ is exactly given by the time constant τ_x evaluated from the exponential function.

(2) The 0D trap with reaction radius=0 (type a) executes a RW in the conventional sense. Particularly, for $\phi=1$ the lattice points are indistinguishable and the RW is symmetric. The curve V_a for $\phi=1$ is also exponential, while for $\phi\neq 1$ it is the superposition of two exponential functions

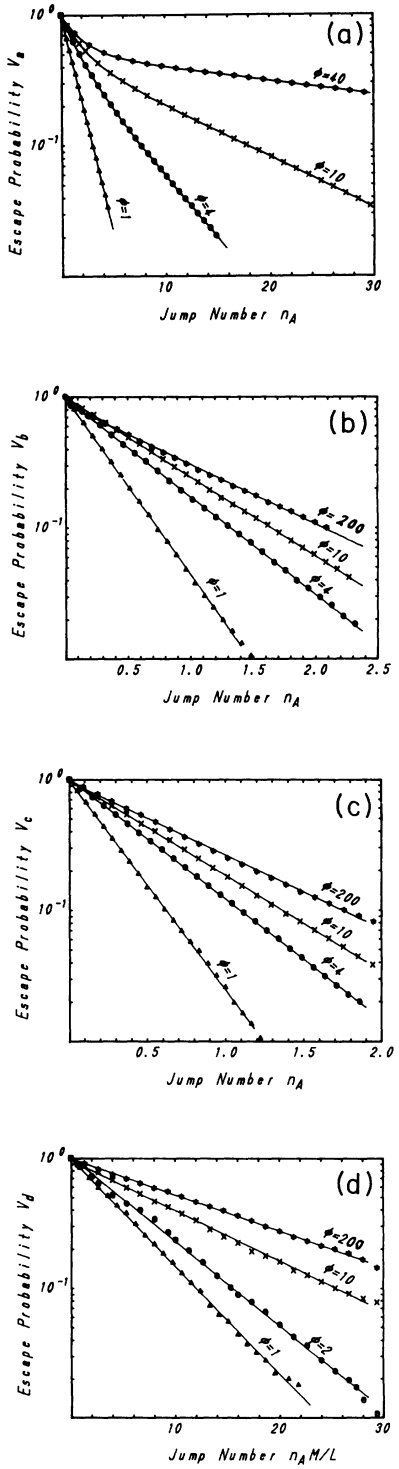

FIG. 2. The escape probability during "isothermal annealing" for alloys with $C_A=C_B$. (a) ideal trapping; (b) 0D trap with reaction radius to NN; (c) 0D trap with reaction radius to NNN; (d) 1D trap with reaction radius to NNN.

$$V_a = A_1 \exp\left[-\frac{t}{\tau_{a1}}\right] + (1-A_1)\exp\left[-\frac{t}{\tau_{a2}}\right]$$
$$= A_1 \exp\left[-\frac{n_A}{\psi_{a1}}\right] + (1-A_1)\exp\left[-\frac{n_A}{\psi_{a2}}\right]$$
$$= A_1 \exp\left[-\frac{n_B}{\psi'_{a1}}\right] + (1-A_1)\exp\left[-\frac{n_B}{\psi'_{a2}}\right], \quad (3.6)$$

as shown in Fig. 2(a). In the case of $C_A = 0.5$ the evaluated ψ_{a1} and ψ_{a2} are listed in Table I. A_1 turns out to be equal to C_A.

(3) The curves of V_d for the 1D trap (reaction radius to NNN) also obey the exponential function [Fig. 2(d)], but here $\ln V_d$ is plotted as function of $n_A M/L$ rather than of n_A

$$V_d = \exp\left[-\frac{t}{\tau_d}\right] = \exp\left[-\frac{n_A M}{\lambda_A L}\right] = \exp\left[-\frac{n_B M}{\lambda_B L}\right]. \quad (3.7)$$

Here L is the number of the lattice sites on the plane normal to the trap, so that M/L is the number of the (110) lattice planes in the sublattice (for a trap in the [110] direction) and λ_A and λ_B the total number of jumps per lattice column during the time τ_d. In contrast to all ψ's, the parameters λ_A and λ_B in this expression depend on the size of the computer crystal used. Figure 3 exhibits the dependence of λ_A vs $\ln L$ for $\phi = 1$, which yields a straight line

$$\lambda_A = \psi_d \ln qL \quad (3.8)$$

with a slope $\psi_d = 0.729$ independent of the size L and an intersect $\psi_d \ln q$, which leads to $q = 0.059$. Furthermore, the simulations show that, unlike ψ_d, the quantity q does not vary with C_A and ϕ but takes a constant value for a given trap structure and lattice. This allows us to separate the dependence of λ_A on the crystal size from its dependence on the other parameters and thus allows us to generalize the results from a finite crystal lattice. ψ_d and $\psi'_d = \lambda_B \ln^{-1} qL$ can then be derived as a function of both C_A and ϕ from λ_A, λ_B for fixed L. The trapping time is obtained

TABLE I. Parameters for the two superposed exponentials for the nonsymmetric random walk with ideal trapping in case of $C_A = C_B$.

ϕ	A_1	ψ_{a1}	ψ_{a2}
1	0.500	1.314	1.314
2	0.519	1.443	2.486
4	0.486	1.545	4.583
10	0.503	1.733	11.019
40	0.501	1.920	42.064

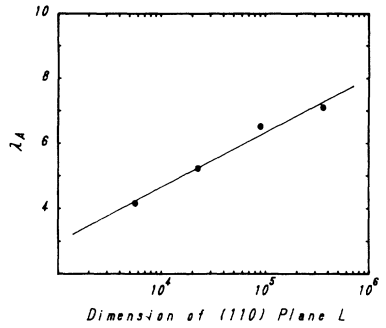

FIG. 3. The dependence of the trapping time on the size of the computer crystal in case of a 1D trap with the reaction radius to NNN. The values for λ_A are obtained by fitting the simulation results to Eq. (3.7).

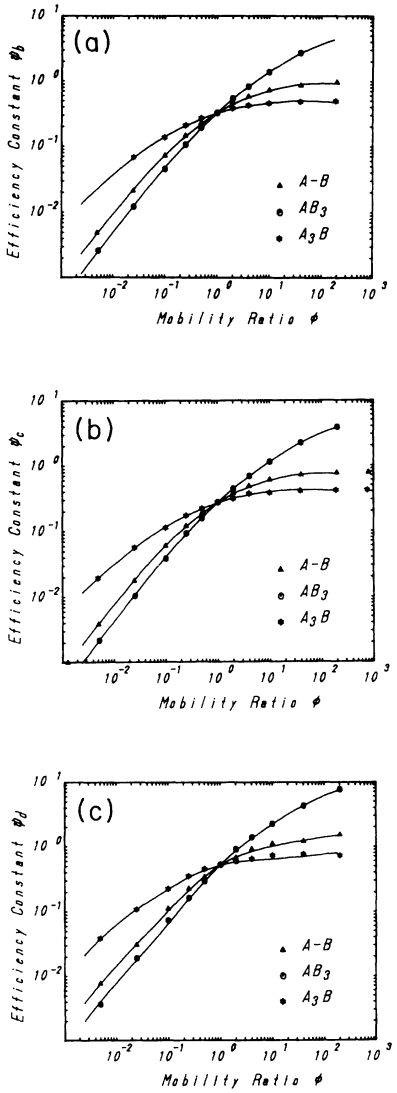

FIG. 4. The dependence of the trapping time on the mobility ratio and the composition. (a) 0D trap with reaction radius to NN; (b) 0D trap with reaction radius to NNN; (c) 1D trap with reaction radius to NNN.

TABLE II. Parameters from fitting the curves in Fig. 4 to Eq. (3.11).

	A	B	C	α	β	γ
ψ_b	0.9241	0.3554	0.081 06	0.4403	0.9527	0.9548
ψ_c	0.7524	0.3393	0.090 47	0.4822	0.9664	0.9656
ψ_d	1.5322	0.3315	0.018 63	0.4748	0.9249	1.2644

$$\tau_d=\frac{\psi_d L\ \ln qL}{\mu_A}=\frac{\psi'_d L\ \ln qL}{\mu_B}\ . \tag{3.9}$$

All ψ_b, ψ_c, and ψ_d, denoting the efficiency constants, have been evaluated by fitting the curves in Fig. 2 to the exponential function and are plotted for various C_A and ϕ in Fig. 4. If ψ_x is written in the form $\psi_x=f_x(C_A-C_B,\phi)$, then due to the symmetry with respect to the two components, we always have $\psi'_x=f_x(C_B-C_A,1/\phi)$ and, because of $\psi_x/\psi'_x=\mu_A/\mu_B=\phi$,

$$f_x(C_A-C_B,\phi)=\phi f_x(C_B-C_A,1/\phi)\ . \tag{3.10}$$

Here $f_x(\xi,\eta)$ is any function of ξ and η. For fitting the resulting curves in Fig. 4, f_x has been selected to have the form

$$f_x(C_A-C_B,\phi)=f_x(0,\phi)\frac{1+\alpha(\phi^h-1)}{1+\beta(\phi^h-1)} \tag{3.11}$$

with $h=\gamma(C_A-C_B)$ and

$$f_x(0,\phi)=\frac{A\phi}{1+\phi}\left\{1-B\exp\left[-C\left[\phi+\frac{1}{\phi}\right]\right]\right\}$$

which fulfills Eq. (3.10). The parameters A, B, and C as well as α, β, and γ in Eq. (3.11) are listed in Table II for different kinds of traps. The solid curves in Fig. 4 are calculated with these parameters. They show a rather good agreement with the points from the simulations.

IV. DISCUSSION

A. The annihilation kinetics

While $V_x(n_A)$ for the nonideal trapping ($x=b,c,d$) obeys identically the simple exponential function, $V_a(n_A)$ for the ideal trapping has the form of two superposed exponential functions. In the latter case the reaction between the PD and a trap, which is also in the form of a lattice point, takes place if the PD and the trap meet together. $1-V_a$ is exactly the fraction of all sites that contribute in the atom motion. The faster exponential corresponds thus to the contribution of the more mobile component and the slower expotential to that of the slower one (Appendix B). The jump of both components is necessary for the migrating trap a to traverse the whole lattice. In contrast to this, the nonideal trapping (with traps b,c,d) has a certain reaction range and the trapping can progress only by the subsequent jumps of the more mobile component without any significant contribution of the sluggish one. This is always realistic for the composition of alloy above the percolation threshold ($p_c=0.198$ for fcc alloys[16]). The simple exponential function indicates that the recovery of PD's is mainly determined by the faster component. The most trap-PD reactions take place within a certain reaction range, and the nonideal trapping is of general significance so that only this will be discussed below.

Since the present simulations have been performed with the technique of migrating traps and "resting" PD's, the periodic sublattice can contain only a single trap so that the trap density cannot be varied directly in any scale for a given lattice. Instead, the trapping time as a function of the size M (or L for 1D traps) of the sublattice, and thus also of the trap density $\rho_{\rm tr}=1/M$ (or $=1/L$), has been studied. For very large sublattice, i.e., $\rho_{\rm tr}\ll 1$, the results must be of general nature. Under this consideration Eqs. (3.4) and (3.9) lead to the general expressions

$$\tau_x=\frac{\psi_x}{\rho_x\mu_A}\quad\text{for 0D}\quad\left[\rho_b,\rho_c=\frac{1}{M}\right], \tag{4.1}$$

$$\tau_d=\frac{\psi_d}{\rho_d\mu_A}\ln\frac{q}{\rho_d}\quad\text{for 1D}\quad\left[\rho_d=\frac{1}{L}\right]. \tag{4.2}$$

According to the first-order reaction for PD trapping found by the MCS's for the nonideal trapping, the rate equation for annealing out of the PD's at trap x has the usual form

$$-\Delta\dot{\rho}_{\rm PD}=\frac{\Delta\rho_{\rm PD}}{\tau_x}\ . \tag{4.3}$$

Here $\rho_{\rm PD}$ is the density of the PD's per atom, $\Delta\rho_{\rm PD}$ the deviation from their equilibrium value and τ_x the trapping time. For one kind of trap and a constant τ_x, Eq. (4.3) describes the first-order annihilation kinetics. If there are several kinds of traps, their contributions to the annihilation rate can be superimposed as follows:

$$-\Delta\dot{\rho}_{\rm PD}=\Delta\rho_{\rm PD}\sum_x\frac{1}{\tau_x}\ . \tag{4.4}$$

For the recovery of surplus vacancies after quenching, two mechanisms appear to be most important in the temperature range about the recrystallization temperature: the annihilation by formation of more mobile divacancy and by absorption at dislocations. If it is assumed that either the dislocations or divacancies as a trap have a reaction zone to the next-nearest neighbors (NNN's), the results from the simulation can then be used directly for this case

$$-\Delta\dot{C}_V=\left[\frac{2}{\tau_c}+\frac{1}{\tau_d}\right]\Delta C_V$$
$$=\mu_A\left[\frac{2C_V}{\psi_c}+\frac{\rho_D}{\psi_d}\ln^{-1}\frac{q}{\rho_D}\right]\Delta C_V\ . \tag{4.5}$$

The reason to introduce the factor 2 is that each time two vacancies disappear for the formation of a divacancy. In the high-temperature range where the concentration of vacancies is high, the recovery of surplus vacancies by the formation of divacancies will dominate, while in the low temperature range the recovery at dislocations may govern. Formally we have the following criterium:

$$\frac{2\psi_d}{\psi_c}\frac{C_V}{\rho_D}\ln\frac{q}{\rho_D}\begin{cases}\gg 1 & \text{divacancy}\\ \ll 1 & \text{dislocation.}\end{cases} \tag{4.6}$$

In case of the dislocation mechanism, the recovery progresses in the form of a simple exponential function. For the divacancy mechanism, however, the trap density and the trapping time varies with the annealing time. For the quenching from a very high temperature, the recovery of surplus vacancies obeys the second-order reaction at the initial periods ($C_V \gg C_V^*$) and turns to the first-order reaction at the end period ($C_V \sim C_V^*$).

B. The activation energies for the recovery of PD's

The activation energy for the recovery of PD's is phenomenologically defined by the Arrhenius-rule

$$H_{\mathrm{PD}}=\frac{d\ln\tau_x}{d(1/kT)}\ . \tag{4.7}$$

If a single annealing mechanism governs, an unambiguous H_{PD} can be conveniently derived by using our simulation results.

(i) For a constant density of traps as dislocation, from Eqs. (4.1) (4.2), and (4.7) it follows

$$H_{\mathrm{PD}}=-\frac{d\ln\mu_A}{d(1/kT)}+\frac{d\ln\psi_x}{d(1/kT)}\ . \tag{4.8}$$

Substituting $H_A^M=-d\ln\mu_A/d(1/kT)$ and $g_x=\partial\ln\psi_x/\partial\ln\phi$ into the above equation, we have

$$H_{\mathrm{PD}}=H_A^M+g_x(C_A-C_B,\phi)(H_B^M-H_A^M)\ . \tag{4.9}$$

Here it is obvious that H_A^M and H_B^M are the migration energy of the components A or B to the considered PD in the alloy.

(ii) For the divacancy mechanism, in this case τ_x varies with the annealing time because of the progressive recovery of surplus vacancies. Considering the behavior at the equilibrium we have

$$\tau_x^*=\psi_x/C_V^*\mu_A\ . \tag{4.10}$$

By substituting this into Eq. (4.7) we obtain, instead of Eq. (4.9),

$$H_{\mathrm{PD}}=-\frac{d\ln\mu_A}{d(1/kT)}+\frac{d\ln\psi_x}{d(1/kT)}-\frac{d\ln C_V^*}{d(1/kT)}\ . \tag{4.11}$$

Since $H^F=-d\ln C_V^*/d(1/kT)$ denotes the formation energy of vacancy, one obtains in this case

$$H_{\mathrm{PD}}=H^F+H_A^M+g_x(C_A-C_B,\phi)(H_B^M-H_A^M)\ . \tag{4.12}$$

For a known $\psi_x=f_x(C_A-C_B,\phi)$ g_x can be calculated. Particularly, for f_x in the suggested form of $f_x(0,\phi)f'(C_A-C_B,\phi)$ in Eq. (3.11) we have

$$g_x(C_A-C_B,\phi)=\frac{1}{1+\phi}+\left[\phi-\frac{1}{\phi}\right]\frac{BC\exp\left\{-C[\phi+1/\phi]\right\}}{1-B\exp\left\{-C[\phi+1/\phi]\right\}}+\frac{h(\alpha-\beta)\phi^h}{\left[1+\alpha(\phi^h-1)\right]\left[1+\beta(\phi^h-1)\right]}\ . \tag{4.13}$$

The function $g_c(C_A-C_B=0,\phi)$ for the trap c is plotted in Fig. 5. Equation (4.13) yields generally $g_x=0$ for $\phi\gg 1$ ($\mu_A\gg\mu_B$). This leads further to $H_{\mathrm{PD}}=H_A^M$ for case (i) and $H_{\mathrm{PD}}=H_A^M+H^F$ for case (ii). This indicates clearly that the more mobile component is mainly responsible for the recovery of the PD's in the case of nonideal trapping.

On the other hand, the last term in Eq. (4.13) describes the dependence of the activation energy on the composition of the alloy. Because of $\alpha-\beta<0$ (Table II) g_x decreases with increasing $h=\gamma(C_A-C_B)$ for ϕ near to 1, so that H_{PD} approaches more closely the value of H_A^M or $H_A^M+H^F$. This means that, concerning the dependence on the composition, for the annihilation of PD's the majority component is more responsible, while in case of the

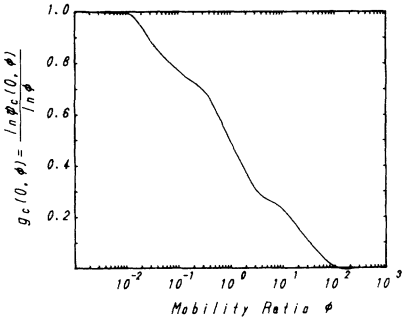

FIG. 5. Relation between the activation energy and the mobility ratio for the 0D trap with reaction radius to NN and $C_A=C_B$.

chemical diffusion the diffusion of the minority component determines the reaction kinetics.

It must be noticed that these statements as well as Eqs. (3.10) and (4.13) themselves may fail totally below the percolation threshold. Effects of the percolation threshold have been discussed in the book of Murch.[17]

C. Comparison to the traditional treatments

A number of computer simulations of the diffusion problem in alloys have been performed by Murch.[13] In his work mainly the tracer diffusion, in particular, the correlation factor for the diffusion coefficient in case of $\mu_A/\mu_B \neq 1$, is of interest. In the present simulation the effort has been undertaken for another topic, i.e., the average survival time of the PD in alloys. The relation between self-diffusion and other diffusion controlled processes is discussed in Ref. 14.

Compared to the models using a noncontinuous approach in this area [the conventional RW considers the case $\mu_A/\mu_B=1$ (Refs. 3 and 4) and the usual treatments by the percolation theory deal with the cases $\mu_A/\mu_B=\infty$ or $\mu_A/\mu_B=0$ (Refs. 15 and 16)], in this paper the general cases of μ_A/μ_B different from 1 have been discussed. Furthermore, the various kinds of trap structures have been taken into account. Concerning the quantitative agreement, only the symmetric RW with ideal trapping is analytically solved in the conventional treatments of the RW theory. This corresponds to the case of the 0D trap with a single-site reaction range and $\phi=1$ simulated here. The result of Rosenstock based on the RW theory gives the trapping time $\tau_{tr}^{-1}=\mu_A/\langle N_{tr}\rangle=(1-F)\rho_{tr}\mu_A$ [Eq. (2.8)], for a fcc lattice with $1-F=0.744$. The present simulation yields $\tau_{tr}^{-1}=\rho_{tr}\mu_A/\psi_{a1}$ with $1/\psi_{a1}=0.763$ (Table I). The agreement is rather good.

Many problems of the PD reaction in solids have been successfully solved by the theory of continuous diffusion. The complete description of the recovery of the PD's comprises the interaction between the lattice imperfections, the mechanisms of the absorption of the PD's at traps and the diffusion of the PD's to the traps. Different models have been developed for all these aspects.[1,5,6] In contrast, the problems like dynamic behavior of PD cannot be simulated by the MC method at all. Furthermore, due to the algorithm of "exchange" of PD and trap, here the periodic sublattice can contain only a single pair of PD and trap, so that the interaction between PD's and the interference between different pairs are fully ignored. As discussed in Refs. 4, 9, and 10, for high trap density (e.g., $\rho_{tr}>0.002$ discussed in Ref. 4) the $V_a(\phi=1)$ curve deviates severely from the exponential function. The present method is thus restricted to moderate trap density.

To check the present method the quantitative comparison to the results from the phenomenological theory of the diffusion model[1,6] is exhibited below. This theory, which yields an analytical expression for reaction constant K contains the following simplifications (general cases without these simplifications are also discussed in Ref. 1).

(1) The interaction between PD's and traps is restricted only to a reaction region with the reaction radius R_0. For a distance larger than R_0 there is no interaction.

(2) PD's will be instantaneously trapped as soon as they reach the reaction region of a trap.

(3) The migration of PD's outside the reaction region is to be described by the diffusion in an isotropic continuous medium.

The reaction constant K, traditionally used for the description of the PD recovery and defined by the rate equation in the form

$$-\Delta\dot{\rho}_{PD}=K\rho_{tr}\Delta\rho_{PD}\,, \tag{4.14}$$

can be derived from the simplifications given above. For the 0D traps we have for the dimensionless trap density[1]

$$K=K_0=\frac{4\pi}{\Omega}D_0R_{tr}\left[1+4\pi\frac{R_{tr}^3}{\Omega}\rho_{tr}+o(\rho_{tr})\right] \tag{4.15}$$

and for the 1D traps (dislocation)

$$K=K_1=\frac{2\pi D_0}{\Omega'}\ln^{-1}\frac{R_D}{R_{tr}}\quad\text{with } R_D^2=\frac{\Omega'}{\pi\rho_D}\,. \tag{4.16}$$

D_0 is the diffusion coefficient of the PD and Ω denotes the volume per atom and Ω' the area per atom normal to the dislocation. R_{tr} is defined as the phenomenological reaction radius of the trap. For symmetric random walk R_{tr} has been calculated analytically for 0D traps we are considering in this paper.[1]

Now the quantity K can also be evaluated from the simulation results by the function $\psi_x=f_x(C_A-C_B,\phi)$ [Eq. (3.11)] as

$$K=\frac{1}{\tau_x\rho_{tr}}=\frac{\mu_A}{\psi_x}\quad\text{for 0D}\,,\quad x=b,c \tag{4.17}$$

and

$$K=\frac{\mu_A}{\psi_d}\ln^{-1}\frac{q}{\rho_D}\quad\text{for 1D} \tag{4.18}$$

[see Eqs. (4.3) and (4.14)].

The comparison of Eq. (4.18) to (4.16) shows that the unknown quantity q in Eq. (4.2) or (3.9) must be equivalent to $\Omega'/(\pi R_{tr}^2)$. The supposition introduced in Sec. III B that q is independent of C_A and ϕ appears to be correct.

For a monoatomic fcc lattice we have $\Omega=a_0^3/4$ and $\Omega'=\sqrt{2}a_0^2/4$ with a_0 being the lattice constant. Inserting these quantities and $D_0=fa^2\mu_A/6=fa_0^2\mu_A/12$ with $f=0.78$ (Ref. 18) into Eqs. (4.15) and (4.16) yields

$$\frac{K}{\mu_A}=\begin{cases}\dfrac{4\pi f}{3}\dfrac{R_{tr}}{a_0}=3.27\dfrac{R_{tr}}{a_0} & \text{for 0D}\\[2ex] \dfrac{2\sqrt{2}\pi f}{3}\ln^{-1}\dfrac{\sqrt{2}}{4\pi\rho_D}\dfrac{a_0^2}{R_{tr}^2}=2.31\ln^{-1}\dfrac{0.11}{\rho_D}\dfrac{a_0^2}{R_{tr}^2} & \text{for 1D}\end{cases} \tag{4.19}$$

TABLE III. K/μ_A from simulations [Eq. (4.17) and (4.18)] and diffusion method [Eq. (4.19)] for mono- atomic lattices.

Type of traps	Ideal trapping	0D/NN	0D/NNN	1D/NNN
Present simulation	0.76	3.10	3.71	$1.30\ln^{-1}(0.06/\rho_D)$
Diffusion method (Ref. 1)	0.62	2.29	2.71	$2.31\ln^{-1}(0.16/\rho_D)$

The values of K/μ_A calculated both from the present simulations by using Eqs. (4.17) and (4.18) and from the treatment with diffusion method [Eq. (19)] are exhibited in Table III, where for the diffusion method the values of R_{tr}/a_0 for the various traps are based on Fig. 6.4 of Ref. 1. In contrast to the good agreement of the result from the present simulations with the analytical solution of the RW method in the case of symmetric RW and ideal trapping, Table III shows a rather poor quantitative agreement. The values of K/μ_A from simulations are about 20% higher than those from the diffusion method. This difference is due to the essential property of the both approaches. In the treatment using RW method all lattice sites are set equivalent, and we always have a homogeneous distribution of PD in the whole lattice. In the derivation of Eqs. (4.15) and (4.16) using the diffusion method, however, the stationary condition is considered, which leads to the distribution of PD from 0 around a trap up to $\rho_{PD,\infty}$ in infinity. In the presence of this gradient the intensity of the PD-trap reaction reduces considerably compared to a homogeneous distribution of PD so that a reduced K is obtained. This indicates that for the problems near the equilibrium the values from the diffusion method by adequately selecting the boundary condition are advisable. For the case far from equilibrium the results from the RW approach should be of sufficient accuracy.

V. SUMMARY

A method to study the trapping of PD by Monte Carlo simulation has been introduced: (1) to simulate the random walk in concentrated alloys by using various compositions of the alloy and various mobility ratios of the components, (2) to simulate traps with complicated structures by using the "fixed" PD and "mobile" trap, and (3) to study the dependence of trapping on the trap density by alternating the size of the periodic sublattice.

From the results of simulations for fcc "random" alloys it has been observed that for the trap with the reaction range of a single lattice the time dependence of the escape probability can be described by two superposed exponential functions, while for traps including NN or more lattice sites it yields the simple exponential function. A set of empirical functions have been evaluated, which describe the dependence of the trapping time on all relevant parameters. Also the activation energy for PD recovery can be derived by directly using these empirical functions. It is shown that for compositions above the percolation threshold the PD annihilation is mainly determined by the more mobile component or by the majority component.

The present results agree well with the analytical solution by RW approach in case of symmetric RW and ideal trapping. The increased reaction constants compared to those from diffusion theory for monatomic lattices are caused by the homogeneous distribution of PD in the whole lattice.

APPENDIX A: CALCULATION OF THE PROBABILITY p_N

The probability for a PD executing RW to be trapped in its Nth jump can be expressed by the product of two quantities,

$$p_N = g_N F_N \ , \tag{A1}$$

where F_N is the probability that the PD survives the first $N-1$ steps and g_N the probability that the PD meets with a trap at its $N$the jump.

For an infinite crystal lattice with a trap density ρ_{tr} we have for the probability of the "survival"

$$F_N = (1-\rho_{tr})^{q_N - 1} \tag{A2}$$

for q_N distinct visited lattice sites during N steps in the finite sublattice (for a sufficiently large sublattice and after sufficient steps we have $q_N \rightarrow \langle S_N \rangle$). Since the PD has the probability $q_N - q_{N-1}$ at its Nth jump to meet with sites never visited before, one obtains on the other hand,

$$g_N = (q_N - q_{N-1})\rho_{tr} \ . \tag{A3}$$

Inserting of both formulas into Eqs. (A1) leads to Eq. (2.5).

For a finite crystal with the dimension of M lattice sites and a single trap site, the probability meeting with an arbitrarily distributed trap by a new lattice site after $N-1$ steps is equal to $1/(M-q_{N-1})$ rather than the constant ρ_{tr} and we get, instead of Eq. (A3),

$$g_N = \frac{q_N - q_{N-1}}{M - q_N} \tag{A4}$$

as well as

$$F_N = \prod_{K=1}^{N-1}(1-g_K) = \prod_{K=1}^{N-1}\frac{M-q_K}{M-q_{K-1}} = \frac{M-q_{N-1}}{M} \ . \tag{A5}$$

For this case we obtain Eq. (2.10).

APPENDIX B: SUPERPOSITION OF TWO EXPONENTIALS IN THE NONSYMMETRIC RW WITH IDEAL TRAPPING

A single PD walks arbitrarily in a finite sublattice composed of M_A sites occupied by A atom and M_B sites by B

atom. It is assumed that during the total N jumps the PD has traversed the whole crystal M times; this means, that the PD has left and then reentered the crystal m times. During its ith stay in the sublattice the PD has made N_i jumps and we have thus

$$N=\sum_{i}^{m} N_i \ . \tag{B1}$$

We now introduce the symbols $q_{i,A}$ and $q_{i,B}$, which will denote the number of the lattice sites initially occupied by an A or B atom and visited by the PD during its ith stay. $q_{i,X}/M_X$ corresponds thus to the probability for a lattice site occupied by an X atom to be visited by the PD during its ith stay. One obtains the number of the distinct visited lattice sites during the ith stay with respect to the total history

$$z_i=q_{i,A}\prod_{j=1}^{i-1}\left[1-\frac{q_{j,A}}{M_A}\right]+q_{i,B}\prod_{j=1}^{i-1}\left[1-\frac{q_{j,B}}{M_B}\right] . \tag{B2}$$

$\prod_{j=1}^{i-1}[1-(q_{j,X}/M_X)]$ describes the probability that a lattice site occupied by an X atom has not been visited by the PD till its ith stays. The survival probability after the total N jumps or the total m stays follows:

$$\begin{aligned} V_N &= 1-\sum_{i=1}^{m}\frac{z_i}{M_A+M_B} \\ &= \frac{M_A}{M}\left[1-\sum_{i=1}^{m}\frac{q_{i,A}}{M_A}\prod_{j=1}^{i-1}\left[1-\frac{q_{j,A}}{M_A}\right]\right] \\ &\quad +\frac{M_B}{M}\left[1-\sum_{i=1}^{m}\frac{q_{i,B}}{M_B}\prod_{j=1}^{i-1}\left[1-\frac{q_{j,B}}{M_B}\right]\right] \\ &= \frac{M_A}{M}\prod_{i=1}^{m}\left[1-\frac{q_{i,A}}{M_A}\right]+\frac{M_B}{M}\prod_{i=1}^{m}\left[1-\frac{q_{i,B}}{M_B}\right] . \end{aligned} \tag{B3}$$

For a sufficient large sublattice $q_{i,A}/M_A \ll 1$ we have

$$\prod_{i}\left[1-\frac{q_{i,A}}{M_A}\right]\approx\exp\left[-\frac{\sum_{i} q_{i,A}}{M_A}\right] . \tag{B4}$$

Since for this case each stay of the PD in the sublattice is relatively long and also $q_{i,A}, q_{i,B} \gg 1$ is valid, we obtain

$$q_{i,A}\approx r_a N_i \ , \quad q_{i,B}\approx r_B N_i \ , \tag{B5}$$

where r_A and r_B means the probability that the PD by the next successful jump meets with a lattice site never visited before. r_A as well as r_B must be thus constant for an infinite large sublattice after sufficient steps. They depend not only on the composition of the sublattice, but also on the mobility ratio of both components. Inserting Eqs. (B4) and (B5) into (B3) yields

$$V_N=C_A\exp\left[-\frac{r_A N}{M_A}\right]+C_B\exp\left[-\frac{r_B N}{M_B}\right] . \tag{B6}$$

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