Suppressed kinetics of short range ordering at low temperatures

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The kinetics of short range ordering in a binary alloy were studied by Monte Carlo simulation. Unlike the kinetics of ordering by the direct interchange of atoms, at low temperatures there is a marked suppression of the kinetics of ordering when ordering occurs by the vacancy mechanism. Large activation energies are associated with this suppression of kinetics. These activation energies suggest that certain heterogeneities in the atomic arrangements on the lattice behave as traps which the vacancy cannot easily escape at low temperatures. Such traps were observed during simulations of the ordering process.

I. INTRODUCTION

At low temperatures, the rearrangement of atoms in many crystalline alloys proceeds by a vacancy mechanism. Given a force law for interatomic interactions, molecular dynamics can be used to calculate the motion of the atoms around the vacancy, from which rates of self-diffusion are obtained.[1] However, for diffusion in concentrated alloys, the large variety of local environments around a vacancy necessitates a simpler approach, and rate theory is frequently used to treat the jump process.[2,3] Rate theories require an activation energy for the diffusive jump, which is the difference between the potential energy of the atom before the jump and at the saddle point of its jump. Calculations of absolute rates for diffusive jumps require nontrivial analyses of attempt frequencies. The problem is simplified if it is recast as a competition between the neighbors of the vacancy to jump into the vacant site, and time averages are taken over many diffusive jumps.

Early analytical treatments of the kinetics of short range ordering in alloys employed a direct connection between changes in short range order parameters and free energy changes in the alloy.[4,5] However, kinetic phenomena are generally sensitive to the mechanism by which change occur. Some success in using vacancies to relate diffusion kinetics and short range ordering was obtained by Radelaar.[6] Vacancies were an integral part of the work by Kikuchi and Sato who, in a series of papers, refined the path probability method and applied it to a study of the kinetics of short range ordering in concentrated alloys.[7–10] Their work demonstrated the importance of the ratio U (definitions of terms are supplied in Table I), which expresses the relative difference in strength of the A atom interactions and the B atom interactions. Only a sum $4V$ determines the equilibrium short range order (SRO), but the saddle point energies depend on the specific bonds to those atoms around the vacancy. In the pair approximation of the path probability method, however, first nearest neighbor correlations were used to average over the different types of atomic configurations around the vacancy.

To keep track of the exact state of the lattice, it is convenient to employ a digital computer. In a Monte Carlo study of diffusion, the heterogeneity of the alloy was found to suppress the tracer correlation coefficient.[11] Tracer correlation coefficients for an ordering alloy were studied as a function of temperature.[12,13] At low temperatures there were large differences in the exchange frequencies of A and B

TABLE I. Definitions.

E^*	saddle point energy without bond energy contribution
V_{AA}, V_{BB}, V_{AB}	bond energies of A–A, B–B, and A–B pairs (energetically favorable bonds have negative energies)
N_{AA}, N_{BB}, N_{AB}	number of A–A, B–B, and A–B bonds to an atom near a vacancy ($N_{BB} \equiv 0$ if the atom is type A)
$4V \equiv V_{AA} + V_{BB} - 2V_{AB}$	thermodynamic ordering energy ($4V > 0$ for ordering alloy)
$V_A \equiv V_{AA} - V_{AB}$	
$V_B \equiv V_{BB} - V_{AB}$	
$U \equiv \frac{V_A - V_B}{4V}$	
$\Delta E \equiv \Delta N_{AA} V_{AA} + \Delta N_{BB} V_{BB} + \Delta N_{AB} V_{AB} = -2V\Delta N_{AB}$	net change in bond energy that results from a direct interchange of atoms

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atoms and the tracer correlation factor was suppressed, presumably because of heterogeneities in the lattice.[13] Early Monte Carlo simulations of short range ordering with a vacancy mechanism were performed by Beeler and Delaney.[14,15] They reported that as SRO developed in the lattice at low temperatures, there occurred a substantial "contraction" of the vacancy mean free path. This simulation, however, used probabilities for the diffusive jump[16] which did not consider the saddle point.

The present work was designed to study the kinetics of short range ordering in a two-dimensional binary alloy by Monte Carlo simulations. At each step of the ordering process, rate theory provided thermodynamic probabilities for a set of allowed atom movements, and a random number was used to select an atom movement from this set. This process continued for many steps, during which statistical data about the state of order in the lattice were obtained. A key goal of this work was to compare the kinetics of ordering by the vacancy mechanism to the kinetics of ordering by the direct interchange of atoms. In many respects there were only quantitative differences between these two mechanisms of atom movement. However, a qualitative difference between the two mechanisms was found in the kinetics of ordering at low temperatures. This difference and its interpretation in terms of vacancy trapping by lattice heterogeneities is the subject of the present report.

II. MONTE CARLO SIMULATION

Monte Carlo simulations employed a two-dimensional square lattice with first neighbor interactions and periodic boundaries. The lattice size was 100×100, and the equiatomic binary alloy was initially random. The simulations ran for up to 3.5×10^7 jumps of the vacancy. Smaller lattice sizes were used to check boundary effects, and different initial configurations (fully ordered and fully clustered) were used to verify thermodynamic reversibility. A set of runs was also performed for an alloy composition of 0.3, but these runs were qualitatively similar to those for the equiatomic case. Rearrangements of atoms took place by two mechanisms. In the first mechanism a single vacant site was introduced into the lattice and one of the four first neighbors of this vacancy jumped into it. The second mechanism involved the direct interchange of the positions of adjacent atoms.

In simulations with the vacancy mechanism, each Monte Carlo step resulted in the jump of one of the four neighbors of the vacancy. A Boltzmann probability p_i was assigned to each candidate jump on the basis of the height of its saddle point energy E_{sp}:

$$p_i = e^{-E_{sp}/kT}, \tag{1}$$

where

$$E_{sp} = E^* - N_{AA}V_{AA} - N_{BB}V_{BB} - N_{AB}V_{AB}. \tag{2}$$

Using the set of four p_i as weights, one of the four candidate jumps was chosen at random. To minimize free parameters E^*, the height of the saddle point without interatomic interactions, was kept the same for all jumps. This led to a common factor for the saddle point of all four candidate jumps that cancelled out when the four jump probabilities p_i were normalized. The saddle point was then determined by the energies and numbers of the A–A, B–B, and A–B bonds, which are denoted as V_{AA}, V_{BB}, V_{AB}, and N_{AA}, N_{BB}, N_{AB}, respectively. The normalized jump probabilities are determined only by the two parameters V_A and V_B (where $V_A \equiv V_{AA} - V_{AB}$, and $V_B \equiv V_{BB} - V_{AB}$, so no loss of generality is incurred by holding V_{AB} equal to 0 as in the present study. Consequently the simulations employing the vacancy mechanism varied only $4V$ and U (where $4V \equiv V_A + V_B$, and $U \times 4V \equiv V_A - V_B$).

In simulations employing a direct interchange of atoms, a nearest neighbor pair was chosen at random. The simulations used the interchange probability I:

$$p = e^{-\Delta E/kT} \quad \text{for } \Delta E > 0$$

or

$$p = 1 \quad \text{for } \Delta E \leqslant 0 \tag{3}$$

or the interchange probability II:

$$p = \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}, \tag{4}$$

where ΔE is the net change in bond energy that would result from the interchange. The direct interchange mechanisms depend only on the variable $4V$ because the interchange of an A–B pair replaces A–A and B–B bonds with an equal number of A–B bonds.

A variety of statistical data were collected during the ordering process, including the distribution of the domain sizes and the surface area of domains as a function of their size. Many of these data will be reported elsewhere. Warren SRO parameters $\alpha(n)$ defined as:

$$\alpha(n) = 1 - \frac{p_{AB}(n)}{c_B}, \tag{5}$$

where $p_{AB}(n)$ is the probability of finding a B atom at a site in the nth neighbor shell of a given A atom, were measured for $1 \leqslant n \leqslant 10$.

III. RESULTS

All five sets of simulations (interchange mechanism simulations with interchange probabilities I or II, and vacancy mechanism simulations with $U = 0$, $U = 0.4$, and $U = 0.8$) were consistent with the well-known critical temperature T_c of $4V/1.76k$. At all temperatures the choice of the interchange probabilities I or II in the direct interchange mechanism had little consequence to the kinetics of short range ordering. However, significant differences in the kinetics of ordering with the different mechanisms were observed, as shown in Fig. 1. (Since the abscissa of Fig. 1 is the interaction energy normalized by kT, it can be read as either the interaction energy or as the inverse temperature.)

At temperatures near T_c the kinetics of short range ordering by the vacancy mechanism are slower by about a factor of two than the kinetics by the direct interchange of atoms. Nevertheless, although the vacancy mechanism is slower than the direct interchange mechanisms, it is not so slow as would be expected if it induced short range ordering primarily by getting two atoms to exchange their positions.

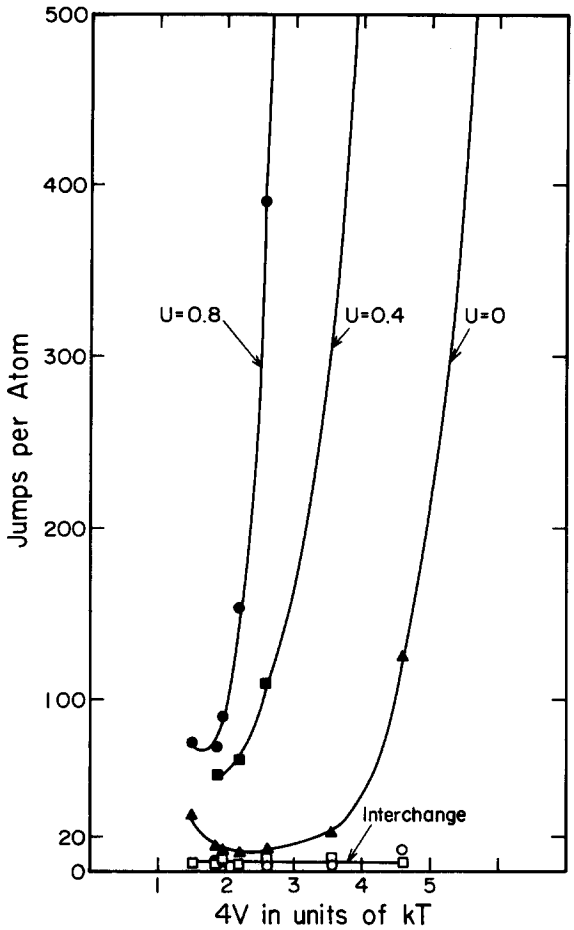

FIG. 1. Number of average jumps per atom required to attain a Warren SRO parameter, $\alpha(1) = 0.25$, vs $4V$. Interchange mechanisms and the vacancy mechanism with $U = 0$, $U = 0.4$, and $U = 0.8$. Lines were drawn to guide the eye.

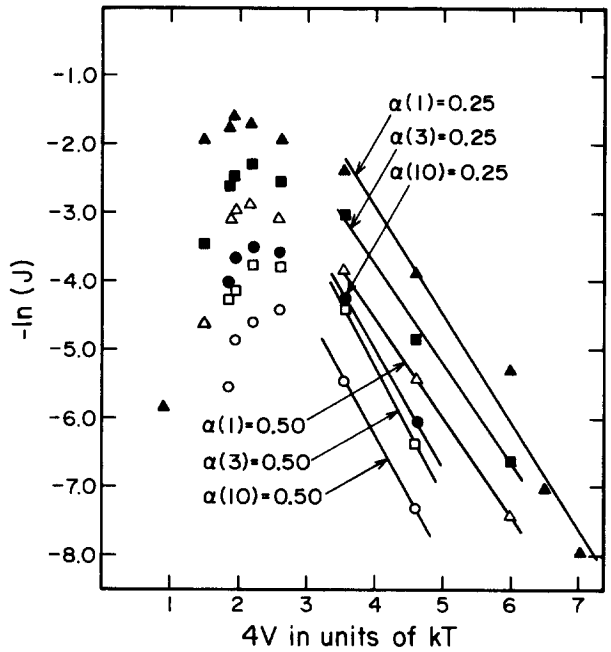

FIG. 2. Semilogarithmic graph of jumps per atom (J) required to attain Warren SRO parameters: $\alpha(1) = 0.25$, $\alpha(3) = 0.25$, $\alpha(10) = 0.25$, $\alpha(1) = 0.5$, $\alpha(3) = 0.5$, and $\alpha(10) = 0.5$, vs $4V$. Vacancy mechanism with $U = 0$. Lines were least squares fit to the low temperature data.

The process of exchanging the positions of a pair of atoms through a coordinated sequence of vacancy jumps is relatively inefficient, especially if the lattice surrounding the pair is constrained to remain unchanged after the exchange. Even locally, the process of ordering with the vacancy mechanism must be understood as involving the cooperative motions of many atoms, and not as pairwise processes.

With the vacancy mechanism, an increasingly greater number of diffusive jumps is required to achieve the same Warren SRO parameters at lower temperatures. This kinetic effect is associated with the vacancy mechanism itself; Fig. 1 shows that this slowing does not occur in simulations employing the direct interchange mechanisms. For the vacancy mechanism, Fig. 2 shows the rates at which the different Warren SRO parameters develop. At low temperatures the slopes of all lines in Fig. 2 are roughly the same. For the other values of U (0.4 and 0.8), these slopes did not depend strongly on the particular Warren SRO parameter or its magnitude. The temperature dependence of the rate at which SRO develops by the vacancy mechanism is shown in Fig. 3 for three different values of U. At temperatures somewhat below T_c, Fig. 3 shows a dependence on U much like that reported by Kikuchi and Sato (Fig. 7 in Ref. 7) for diffusion on a bcc lattice. At temperatures near T_c and higher, Figs. 2 and 3 show that the process of short range ordering slows down, and as expected, at temperatures above T_c the lattice did not achieve large Warren SRO parameters.

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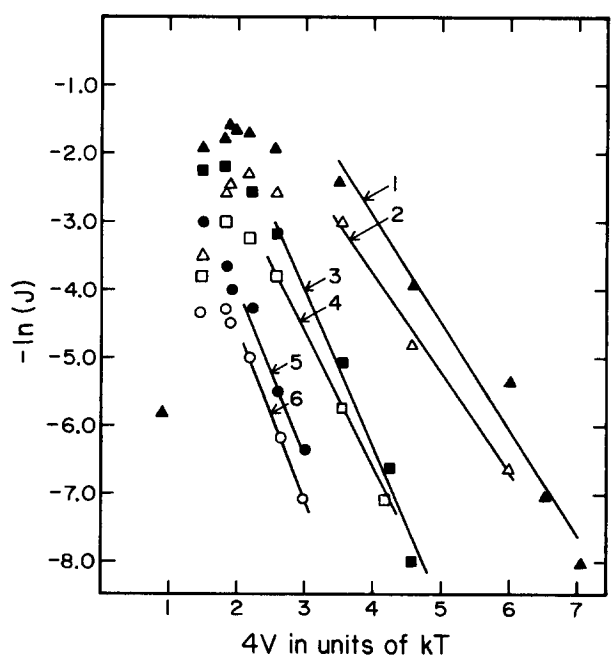

FIG. 3. Semilogarithmic graph of jumps per atom (J) required to attain specific Warren SRO parameters vs $4V$. Vacancy mechanism. Curve (1) $\alpha(1) = 0.25$, $U = 0$; (2) $\alpha(3) = 0.25$, $U = 0$; (3) $\alpha(1) = 0.25$, $U = 0.4$; (4) $\alpha(3) = 0.25$, $U = 0.4$; (5) $\alpha(1) = 0.25$, $U = 0.8$; (6) $\alpha(3) = 0.25$, $U = 0.8$. Lines were least squares fit to the low temperature data.

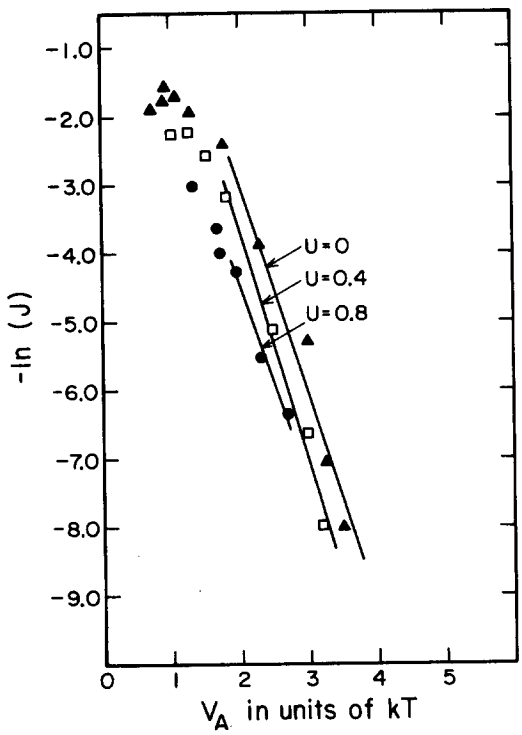

FIG. 4. Semilogarithmic graph of jumps per atom (J) required to attain a Warren SRO parameter, $\alpha(1) = 0.25$, vs V_A. Vacancy mechanism with $U = 0$, $U = 0.4$, and $U = 0.8$. Lines were least squares fit to the low temperature data.

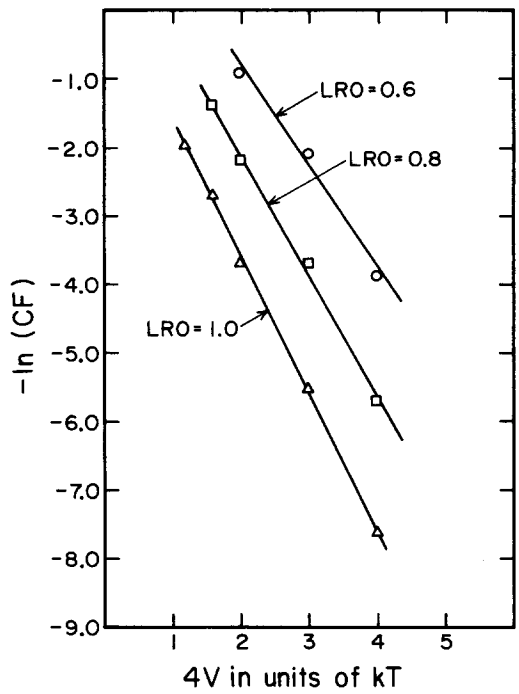

FIG. 5. Semilogarithmic graph of the Beeler and Delaney contraction factor (CF) (Ref. 14) vs $4V$. For 10^6 jumps of the vacancy and initial long range order (LRO) of 0.6 (top), 0.8 (middle), and 1.0 (bottom). Lines were least squares fit to the data.

low temperatures, however, that is the main topic of the present report. Watching the vacancy motion on a video display terminal showed that the "constriction" in vacancy mean free path reported by Beeler and Delaney[14] and Beeler[15] was primarily due to the vacancy being trapped in a few sites of the lattice. The vacancy would shuttle back and forth between these few sites (usually two or three) for hundreds of jumps. When the vacancy escaped from this trap, it diffused irregularly over a large area until it became trapped again. A wide variety of local atomic configurations were found to serve as traps of varying degrees of effectiveness. The trapping phenomenon took on a kinetic importance below temperatures of about T_c when $U = 0.8$. When $U = 0$, however, the kinetics were influenced by trapping when T was less than about $0.5T_c$. [A similar sort of trapping was observed in clustering alloys (i.e., $4V < 0$) during intermediate stages of two-phase decomposition; the vacancy tended to confine itself to a single cluster so that it would not remove interfacial atoms from their preferred cluster.]

An overall activation energy is associated with the trapping process. Activation energies were determined from the average slopes of the lines in Fig. 3, and are $1.51 \times 4V$ for $U = 0$, $2.15 \times 4V$ for $U = 0.4$, and $2.60 \times 4V$ for $U = 0.8$. These activation energies are in the ratio 1:1.43:1.72. This ratio is close to the ratio 1:1.4:1.8, which is the ratio of the energies V_A at the same value of $4V$ for $U = 0$, $U = 0.4$, and $U = 0.8$, respectively. We, therefore, expect the slopes of the lines in Fig. 3 to scale with V_A; this is shown in Fig. 4 which provides an average activation energy of $3.1V_A$. The contraction factor reported by Beeler and Delaney[14] is the ratio of the number of sites visited by the vacancy in the ordering alloy to the number of sites visited by the vacancy in a random walk. The contraction factor has a temperature dependence similar to the data of Fig. 2. Some data of Beeler and Delaney[14] are presented in Fig. 5. The average slope of these data is $1.75 \times 4V$, which corresponds to an activation energy of $3.5 \times V_A$. Considering the difference in jump probabilities and the possible statistical errors, this seems in satisfactory agreement with the present results.

IV. DISCUSSION

The motion of a vacancy through a lattice can be treated as a path over a surface of potential energy barriers. (These potential energy barriers are, however, not constant in time as they change with the motion of the vacancy.) In an alloy with disorder, the vacancy can encounter two or more successive lattice configurations that have a much lower activation barrier between them than the barrier separating them from other nearby configurations. At least two local lattice configurations are needed in order to form a trap. Figure 6 shows a pair of local lattice configurations with a high probability of following each other in the sequence of vacancy jumps when V_A is high and the temperature is low. Entries and exits of the vacancy into this trap must proceed by the passage of the vacancy through six sites, two of which are depicted in Fig. 7. These six entry/exit sites have 14 connections to the untrapped lattice; these connections tend to serve as one-way valves for controlling the flow of vacancies into the traps. Complex traps can be designed with more entry/exit connections or with entry/exit connections in series, but in the following we consider how many vacancy jumps will occur between the two configurations of Fig. 6 (denoted as the trapped state "j").

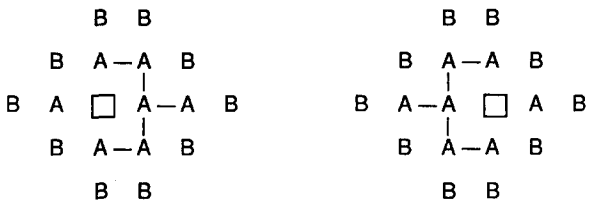

FIG. 6. A pair of local lattice arrangements which comprise a strong vacancy trap when V_A is large and $U = 1$.

To estimate the fraction of vacancy jumps which lead into the trap shown in Figs. 6 and 7, we start with an ensemble of disordered lattices with a random initial location of the vacancy. When we take a random sampling of all possible jumps of the vacancy, the jumps have the geometrical probability p_g that they will end in an entry site of the trap. For a fully disordered lattice, we can use combinatorics to find p_g for the trap of Figs. 6 and 7. The probability p_g depends on the vacancy jump being one of the 14 entry jumps, where for each entry jump there must be 17 atoms properly configured around the entry/exit site. If the lattice is random, $p_g = 1.1\times10^{-4}$ when $c = 0.5$. For simplicity we have assumed no energetic bias for the vacancy to enter an entry/exit site from outside the trap (viz. the vacancy "happens upon" the trap), so the probability for entering the trap W_{ij} is 1/4. The rate of change of the fraction of untrapped vacancies f_u due to vacancies entering these traps is controlled primarily by how many vacancies are near an entry/exit site of a trap:

$$\frac{d}{dt}f_u = -p_g W_{ij} f_u. \tag{6}$$

Once the vacancy is in the trap or is in an entry/exit site, the probability that it will leave the trap W_{ji} is small. The loss of vacancies from the trap of Figs. 6 and 7 requires two jumps which have low probabilities. In the case when $U = 1$, these two probabilities W_{ji} are the same:

$$W_{ji} = \frac{e^{-2V_A/kT}}{3e^{-2V_A/kT}+1}. \tag{7}$$

The rate of change of the fraction of trapped vacancies f_t due to vacancies leaving the trap is

$$\frac{d}{dt}f_t = -(W_{ji})^2 f_t. \tag{8}$$

In equilibrium, the rate of release of trapped vacancies will equal the rate of capture of untrapped vacancies, so

$$(W_{ji})^2 f_t = p_g W_{ij} f_u. \tag{9}$$

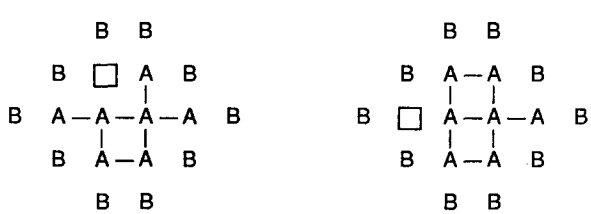

FIG. 7. Two of the six entry/exit points of the trap shown in Fig. 6.

If we define substantial trapping to have occurred when $f_t = f_u = 1/2$, and if we assume the lattice to remain random when equilibrium is achieved, we can use our expression for p_g to find the highest temperature at which substantial trapping occurs: $V_A = 2.6kT$, which corresponds to $2/3T_c$ when $U = 1$. Upon comparison with Figs. 3 and 4, this seems only about two-thirds of the temperature at which trapping is significant. Other traps of different strengths, geometrical probability, and complexity contribute to the vacancy trapping at low temperatures, so this discrepancy is not unreasonable. During short range ordering, it seems that most of the trapping is due to weaker traps than those of Figs. 6 and 7; the activation energy as obtained from the slope of the data shown in Fig. 4 is $3.1V_A$, and the activation energy required for the vacancy to escape the trap of Figs. 6 and 7 is $4V_A$. Weaker traps were, in fact, the usual ones identified when the vacancy motion was followed visually.

The geometrical probability of a trap p_g will change during the course of ordering, so the degree of vacancy trapping will change as order develops in the lattice. It seemed that the amount of vacancy trapping became greater as more order developed in the lattice (see also Fig. 19 in Ref. 14). One reason for this is that a region of ordered lattice makes a strong vacancy trap, as shown in Fig. 8. This configuration of atoms is combinatorically unlikely during the early stages of ordering, but becomes more probable as order develops. When $U = 0$, the vacancy jumps leading from Figs. 8(a) to 8(d) can be the most probable path. Once inside the trap, the vacancy will tend to jump between its site in Fig. 8(d) and one of the four symmetrically equivalent positions of Fig. 8(c). When $U = 1$ the activation energy needed to escape this trap is $4V_A$, which is relatively large.

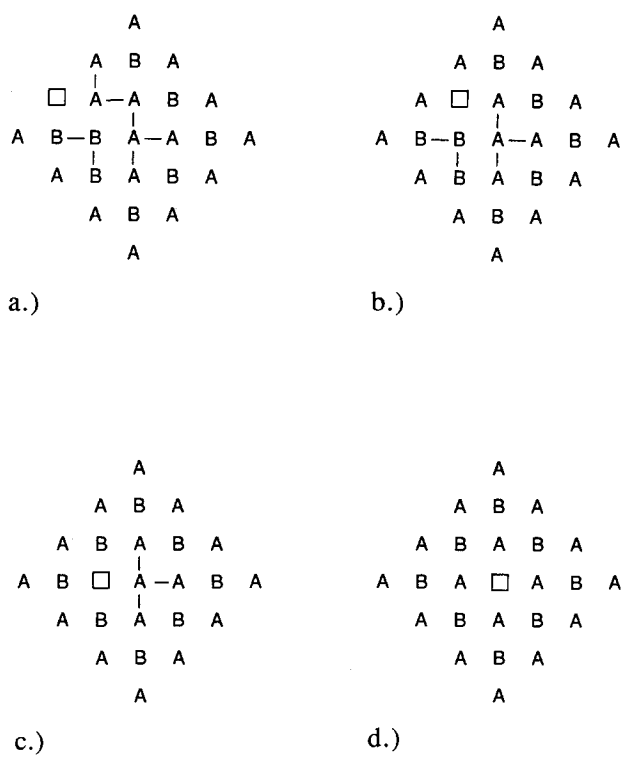

FIG. 8. A vacancy trap in a region of mostly ordered lattice: (a) an entry site, (b) an intermediate site, (c) and (d) sites of strongest trapping.

The present algorithm for the diffusive jump, while providing the correct fraction of jumps in the trap, does not estimate the fraction of time that the vacancy is in the trap. At low temperatures, the time per jump of the central atom in the vacancy trap of Fig. 6 is greater than the average time per jump by a factor of about $\exp(-3V_A/kT)$. This factor, when multiplied by the ratio f_t/f_u, still provides a temperature dependence for trapping that is greater than $\exp(-V_A/kT)$. On the other hand, for the ordered region traps, the jump from Fig. 8(d) to 8(c) is not expected to occur rapidly, and at low temperatures the fraction of time that the vacancy spends in the trap is actually greater than the fraction of vacancy jumps in the trap.

The problem of the kinetics of short range ordering with a vacancy mechanism is inherently more complicated than the equilibrium thermodynamics of ordering, which requires only the parameter $4V$. The path probability method in the pair approximation had previously demonstrated the importance of the ratio U to the kinetics of short range ordering. The present Monte Carlo simulations have roughly verified this dependence at temperatures where trapping is not significant. At lower temperatures, however, the dependence on U becomes more substantial. The vacancy trapping phenomenon was found to depend on V_A, but this does not add a new parameter to the kinetics since V_A is readily obtained from $4V$ and U. Traps are specific configurations of atoms, and the more atoms required to construct a trap, the fewer the number of traps. Strong traps should be most easily formed in lattices with low coordination numbers and interatomic interations which are short ranged.

V. CONCLUSION

During ordering at temperatures less that T_c in the two-dimensional square lattice, the motion of a vacancy was found to become intensely correlated. This correlation is an effect of the vacancy being trapped among a set of lattice configurations having a lower saddle point energy between them than is required for escape to another lattice configuration. The activation energy associated with the fraction of vacancy jumps in the traps was found to be $3.1V_A$, and the activation energy for the fraction of time in the traps was estimated to be larger than V_A. These large activation energies suggest that the traps of greatest significance to kinetics are strong ones. Strong traps were in fact found when observing the vacancy motion.

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