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CORRELATED-UNCORRELATED REACTION KINETICS IN A DISCRETE LATTICE

James W. Corbett
General Electric Research and Development Center, Schenectady, New York
and Physics Department,* State University of New York, Albany, New York 12203

(Received 26 July 1968)

A new technique is introduced which provides a unified formalism for treating diffusion-controlled reaction kinetics in a discrete lattice. Illustrative calculations are presented for vacancy-interstitial reactions in a fcc lattice.

Diffusion-controlled reaction kinetics were first treated by Smoluchowskii.[1] His treatment has been extended and applied in a number of fields, but we will be concerned with radiation damage where such an approach to the recombination kinetics of vacancy-interstitial (Frenkel) pairs was first employed by Fletcher and Brown.[2] The theory was developed in a unified, closed form by Waite,[3] whose work has been extended by others.[4-8] The theory, particularly in the Waite form, has found a number of applications in both semiconductors[5,9-13] and metals,[7,8,14-20] with probably the most extensive test coming in copper.[7,8,14,17] The Waite theory, and its derivatives, has the deficiency of being a continuum theory, whereas the experiments are on discrete lattices which exhibit well-resolved recovery stages.[21] Thus the theory has limited utility in aiding in the identification and the understanding of specific defect configurations and recovery mechanisms. Moreover, the theory employs a spherically symmetric function for the distribution of the interstitial about the vacancy, whereas numerous experiments indicate an anisotropy in the damage threshold and production rate[22] which should be manifest in the distribution function of the interstitials as well. Further, an important parameter obtained from fitting the theory to experiment, the volume about a vacancy for the capture of interstitials, seems too large[14,17,18,20,24] (containing well over 500 lattice sites) in view of both the calculation by Johnson,[25] which gave a capture volume of less than 50 lattice sites, and the observation of relatively few recovery stages due to bound vacancy-interstitial pairs.[21]

In this paper we consider a new computational technique and demonstrate its use in treating diffusion-controlled reaction kinetics in discrete lattices. For convenience, but with no significant detriment, we consider the vacancies immobile and the interstitials the mobile defect. We let $\vec{C}$ be a vector,[26] the ith component of which, C_i, will be the concentration of interstitials at the ith site about a vacancy site; $(C_i)_0$ will be the initial distribution. We let P be the matrix whose components P_{ji} are the probabilities per time increment for transition from the ith to the jth site,[27,28] where the time increment (which we refer to as a "jump") is chosen so that the P_{ji} are conveniently small. The absorbing boundary condition at the sites on the surface of the vacancy capture volume requires $P_{ji} \equiv 0$ for transitions out of the capture volume. Next we establish a hierarchy of difference equations: After the first jump the concentration vector is $\vec{C}_1 = \mathsf{P}\vec{C}_0$; the second jump, $\vec{C}_2 = \mathsf{P}\vec{C}_1 = \mathsf{P}^2\vec{C}_0$; $\cdots$, $\vec{C}_N = \mathsf{P}^N\vec{C}_0$. Thus far we have simply described the well-known matrix technique for handling Markov processes.[29,30] Fletcher and Brown[2,31] in essence used this approach to treat the kinetics of the correlated recovery process, that is, recovery in which the interstitial recombines with its own vacancy.[32]

In general, this recovery exhibits the hallmark of diffusion processes—an initial $\sqrt{t}$ dependence—and is independent of the total concentration of defects. (In this concentration independence, and in this only, correlated recovery kinetics resembles first-order recovery kinetics.)

In this form the matrix technique cannot treat the process where the interstitial "escapes" from its own vacancy and recombines with a "foreign" vacancy—the uncorrelated recovery.[2] Physically this deficiency is due to each vacancy being treated independently; mathematically it manifests itself in the linearity of the terms $P_{ji}C_i$ in the difference equations.

We may readily modify the matrix technique to correct this deficiency. We employ a finite matrix as above. The first l sites belong to the vacancy's capture volume; the next k sites are the sites in the correlated recovery volume; then additional vector components are added for the uncorrelated recovery, one for each physical process which occurs. For the latter processes we require that the P_{ji} be such that the difference-equation terms have the correct physical dependence. Thus for the bimolecular recovery characteristic of uncorrelated vacancy-interstitial annihilation, the pertinent P_{ji} for return to the correlated region are proportional to the concentration of interstitials in the uncorrelated region and so on for interstitial agglomeration, trapping by impurities, etc.[33] Since the progress of the recovery is followed as a function of time, or "jumps," by successive matrix multiplications, this modification of the matrix technique requires only that the special P_{ji} be recalculated before the multiplication is carried out, which is a trivial additional step for the computer. The major computational hazard in this type of calculation is "round-off errors," but, with modern computers, test calculations for known simple kinetics can readily demonstrate that this is a surmountable problem.

Figure 1 shows the results of illustrative calculations of vacancy-interstitial reactions in a fcc lattice. ($\vec{C}^*$ is the concentration of interstitials outside the capture volume.) The curves show an initial correlated recovery, then a plateau corresponding to the asymptotic escape from the correlated region,[34] followed by bimolecular recovery (the only uncorrelated recovery included in these calculations). These and other calculations show that for a given lattice, the shape of the correlated recovery and the height of the plateau are determined mainly by the size and shape of the capture volume surrounding the vacancy and by the distribution of the interstitials with respect to the vacancy; the larger the capture volume and the closer the interstitials are to the capture surface, the fewer the interstitials that escape the correlated region.

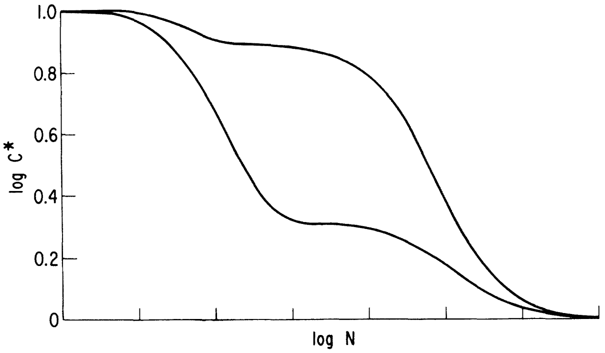

FIG. 1. The results of illustrative calculations of vacancy-interstitial reactions in a fcc lattice. The curves refer to different vacancy capture volumes and interstitial distributions. (C^* is the concentration of interstitials outside the capture volume; N is the number of jumps.)

The modified matrix technique provides a compact formalism for treating a large number of nonlinear coupled differential equations and as such should be readily applicable to a variety of complicated kinetic problems. Here we have shown that it is a unified technique for treating correlated-uncorrelated recovery kinetics in a discrete lattice.

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[28] If required, a vector component could equally well represent the concentration in a collection of sites, e.g., the sites in a shell about the radius. In this case the P_{ji} reflect the transitions for the whole shell. Care must be taken, however, since simple enumeration of the sites associated with a shell can lead to spurious results in the recovery.

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[33] By having $P_{ji} \propto C_i^{(\gamma-1)}$, the term $P_{ji}C_i$ in the difference equation will be $\propto C_i^{\gamma}$ for any desired order (γ) of the reaction kinetics.

[34] The size of the correlated region is chosen such that this asymptote is essentially independent of the size.

SYMMETRY OF ELECTRON STATES IN GaP

Thomas N. Morgan
IBM Watson Research Center, Yorktown Heights, New York

(Received 2 July 1968)

We show that the symmetry of bound electron states in GaP depends upon the choice of origin for the group operations and hence upon the location of impurity in the crystal lattice. This provides an explanation of the discrepancy between the high radiative efficiency associated with group VI donors and group V isoelectronic centers and the low efficiency of group IV donors (Si) in GaP.

Shallow donor states may be introduced into GaP by S, Se, or Te impurities substituting for a P atom or by Si and (possibly) C substituting for Ga.[1] Both types of impurities contribute extrinsic electrons.[1] However, high radiative efficiencies—from donor-acceptor pairs[2] and donor-to-valence band transitions[3]—have been reported only for donors located on P sites. Strong emission has been observed from donors on Ga sites only when a deep impurity state is involved.[4,5] In addition, numerous neutral centers occur on P sites and produce strong emission and absorption,[6] while no such centers on Ga sites have been identified. It is the purpose of this Letter to point out that the selection rules which govern these radiative transitions can be predicted on the basis of the band symmetry alone.

We show that for valleys at the zone edges the representation X_1 or X_3 to which the conduction band minima belong depends upon the choice of