

## Simple ballistic model for vacancy migration

J. A. Van Vechten\*

Bell Laboratories, Murray Hill, New Jersey 07974

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A simple ballistic model for vacancy migration is presented. An expression for the enthalpy of migration in terms of the interatomic spacing and Debye temperature is derived and evaluated for 62 elemental crystals. Calculated values agree with measured values within 15% for the 11 close-packed crystals where data were found. For Si and Ge they equal high-temperature measurements. The model explains the anomalous suppression of the low-temperature migration process near the melting points of Si and Ge.

Even for the simplest cases, such as the noble-gas solids, attempts to calculate the enthalpy of single-vacancy migration  $\Delta H_m(V)$ , the enthalpy of vacancy formation  $\Delta H_f(V)$ , and the activation enthalpy for self-diffusion via a single vacancy process

$$Q(V) = \Delta H_f(V) + \Delta H_m(V) \quad (1)$$

from atomic parameters, have attained only erratic success.<sup>1</sup> One would expect calculations of  $\Delta H_f(V)$ , which involves an equilibrium state, to be simpler and more accurate than calculations of  $\Delta H_m(V)$ , which involves a dynamic process. For many materials of practical interest, such as semiconductors, attempts to calculate even  $\Delta H_f(V)$  from first principles, have been disappointing to the point of predicting the wrong sign.<sup>2,3</sup>

In order to attain a reasonably quantitative description of  $\Delta H_m$  for a range of crystals and to understand chemical trends, it has been necessary to resort to highly simplified models which make use of some empirical macroscopic parameters of the normal crystal such as the Debye temperature  $\Theta$  or the elastic constants. The most successful of these previous models seems to be that of Glyde<sup>4</sup> and Flynn<sup>5</sup> (GFM), which is developed in terms of the "dynamical" theory of diffusion.<sup>6</sup> The present ballistic model (BM) is developed in terms of the "absolute-rate" theory of diffusion.<sup>7</sup> While it has been shown that the dynamical and absolute-rate formalisms are nearly equivalent,<sup>8</sup> the present BM is quite distinct from the GFM in its description of the physics of the vacancy migration process. Moreover, the BM offers an explanation for the fact that in Si and Ge the extrapolation of low-temperature measurements<sup>9,10</sup> of the vacancy diffusivity  $D_v$  to high temperatures exceed the absolute values measured<sup>11,12</sup> at such temperatures<sup>13</sup> (see Fig. 1). The GFM has produced no explanation of this striking anomaly. This situation in Si and Ge is strikingly different from other cases, e.g., Na,<sup>14</sup> where multiple processes contribute additively to self-diffusion. One must conclude that the low-temperature process in Si and Ge is somehow sup-

pressed by high lattice temperatures.<sup>13</sup>

The ballistic-migration process is illustrated schematically in Fig. 2. In Fig. 2(a) we see a close-packed array of spherical atoms with a vacancy. Suppose that the shaded atom is to move directly into the vacant lattice site. It is necessary that the two atoms butting against the shaded, mobile atom move apart as indicated. Supposing the atoms to be more or less hard spheres, as in a Lennard-Jones model, it is evident that the butting atoms need not move very far in the direction indicated before the mobile atom can travel towards the vacant lattice site almost as a free particle [see Fig. 2(b)]. However, the mobile atom must move from its original position  $r_0$  to the midpoint or saddle point  $r_s$  of its migration before the restoring forces acting on the butting atoms repel them back to a point where they will again prevent the mobile atom from passing into the vacancy cavity. Therefore, the time allowed for the ballistic migration of the mobile atom is only about  $\frac{1}{2}$  the period  $\tau_m$  of the butting atoms in this particular "migration" mode. Thus, the velocity of the mobile atom must be

$$\dot{r} = d/\tau_m, \quad (2)$$

where  $d$  is the distance that the mobile atom jumps (here taken to be the interatomic spacing in the perfect crystal), and

$$\Delta H_m(V) = \frac{1}{2} M \dot{r}^2 + h/\tau_m, \quad (3)$$

where  $h$  is Planck's constant and  $M$  is the mass of the mobile atom. The second term represents the phonon energy of the butting atoms in the migration mode and is negligibly small compared with the first term because the amplitude of their vibration is not large. Thus, we approximate

$$\Delta H_m(V) = \frac{1}{2} M \dot{r}^2. \quad (4)$$

Evidently, the use of Eqs. (2) and (4) will produce an underestimate of  $\Delta H_m(V)$  because (a) the fraction of the phonon period  $\tau_m$  during which the mobile atom can pass must be less than  $\frac{1}{2}$ , and (b) the mobile atom will experience some potential in the

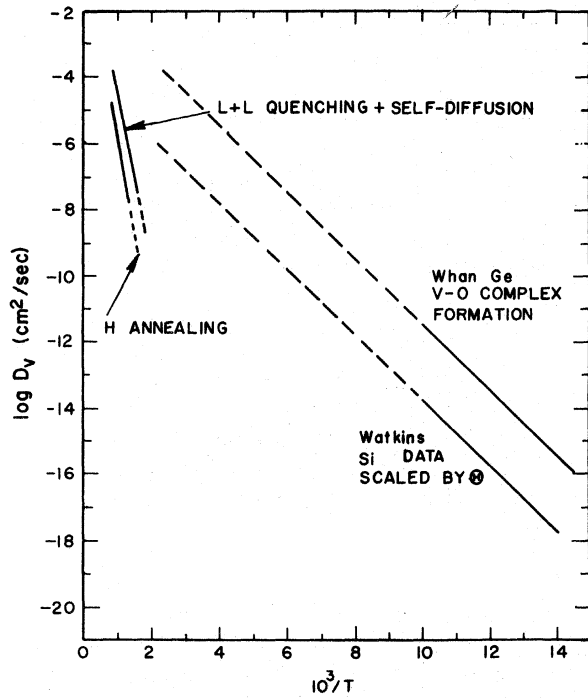


FIG. 1. Anomaly of single-vacancy diffusivity in Ge. Si case is similar. High-temperature measurements, Ref. 12, are less than the extrapolation of Whan's low-temperature measurements, Ref. 10. As Whan's value for the preexponential factor is somewhat imprecise, the accurate Si measurements of Watkins are scaled by the relative  $\Theta$ 's and plotted for comparison

saddle point region around  $r_s$ , which will cause it to slow down requiring a greater initial velocity to complete the motion in the time allowed. In keeping with the rate theory<sup>7</sup> and the assumption that the repulsive interatomic forces vary with a large exponent of interatomic spacing, the repulsive potential is taken to be abrupt, short ranged, and almost equal to  $\Delta H_m(V)$  at  $r_s$  in Fig. 2(b). [Of course, if the butting atoms experience a larger amplitude vibration, the mobile atom may pass without ever contacting them, but this would be a migration mode of higher energy and would not determine  $\Delta H_m(V)$ .]

In order to estimate  $\tau_m$ , note that a normal-mode decomposition of the migration mode of the butting atoms will emphasize a particular zone-boundary phonon, or, for a lattice with a basis, a particular optic phonon. As the atomic motion is perpendicular to the direction of migration and tangential to the surface of the vacancy, it seems likely that this mode will have approximately the same frequency as in the perfect crystal. The particular phonon corresponding to  $\tau_m$  will vary with crystal structure and for anisotropic crystals, like Se and Te, may vary with the direction of migration. Let us leave such refinements to future study and adopt

here the Debye approximation

$$\tau_m = h/k\Theta, \quad (5)$$

where  $k$  is Boltzmann's constant and  $\Theta$  is the Debye temperature of the perfect crystal.

Now the use of Eq. (5) will produce an underestimate of the true period of the zone-boundary or optic phonon<sup>15</sup>  $\tau_m$ . This will produce an overestimate of  $\Delta H_m(V)$  which will compensate to some extent the underestimate produced by Eqs. (2) and (4) noted above. Let us finally take

$$\Delta H_m(V) = \frac{1}{2} M(Fdk\Theta/h)^2, \quad (6)$$

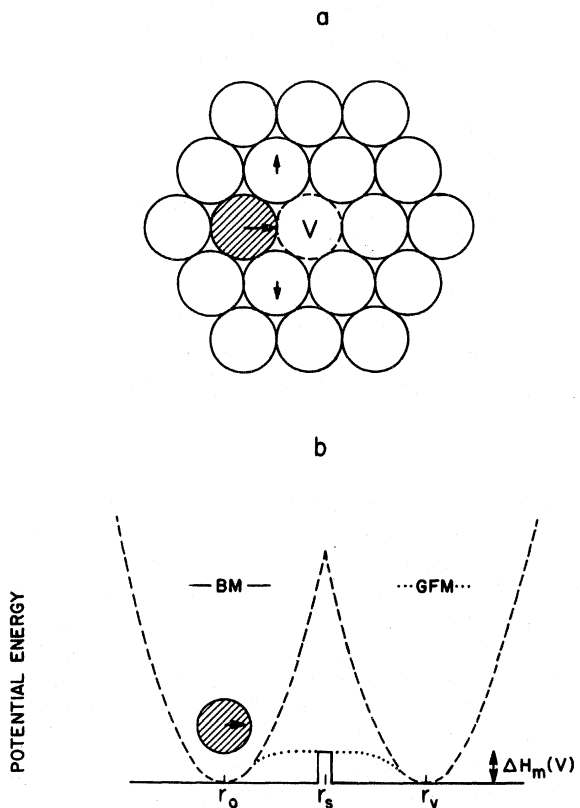


FIG. 2. (a) Schematic illustration of simple-ballistic process: close-packed array with vacancy  $V$  and mobile atom (shaded). Butting atoms must move apart for migration to occur. (b) Assumed potential energy versus position of mobile atom along reaction coordinate for two models. In the present "rate-theory" ballistic model, the mobile atom moves as a free particle, except for a small region between the butting atoms, during the half-period of the phonon during which the butting atoms are spread. During the other half-period, the barrier potential around  $r_s$  is too high for the mobile atom to pass. The "dynamical-theory" model of Refs. 4 and 5 assumes a time-invariant effective potential which is derived from the superposition of harmonic potentials fitted to the elastic constants of the bulk crystal by assuming a smoothing of the resulting cusps at a structure-dependent fraction, 0.067 to 0.104, of the cusp height.

where  $F \sim 1.0$  may be treated as an empirically adjusted, structure-dependent parameter used to correct the residual error between Eqs. (2) and (5). In Table I we see the values calculated with Eq. (6) for the elemental crystals using the values of  $d$  and  $\Theta$  given in Ref. 15 and fixing

$$F(\text{bcc}) = 0.8 \quad (7)$$

for body-centered-cubic crystals and

$$F(\text{fcc}) = F(\text{hcp}) = 0.9 \quad (8)$$

for face-centered-cubic and hexagonal-close-packed crystals by reference to Franklin's "best experimental values" for metals.<sup>16</sup> The fcc value of  $F$  was also used to calculate the values shown in Table I for the diamond and other structure crystals. The empirical values of  $F$  in Eqs. (7) and (8) seem physically reasonable in the BM. The values calculated for the noble-gas solids are found to be in excellent agreement with values obtained by subtracting measured values<sup>17</sup> of  $\Delta H_m(V)$  from measured values<sup>18</sup> of  $Q(V)$ .

It should be noted that while calculated values of Se and Te have been included in Table I for the sake of completeness, they are likely to be inaccurate due to the anisotropy of these structures. An empirical estimate of  $\Delta H_m(V)$  for Te (Ref. 19) is about 50% greater than the calculated value. Rather than simply assuming  $F(\text{Te}) = 1.1$ , one should take proper account of the symmetry and phonon modes of these structures.

Now Eq. (6) is the same as that obtained by Glyde<sup>4</sup> and essentially equivalent to that obtained by Flynn<sup>5</sup> for the GFM, which is also illustrated in Fig. 2(b). They apply the dynamic theory<sup>6</sup> and consider the mobile atom to move in a particular anharmonic potential. No special attention is given to the motion of the butting atoms. The potential seen by the mobile atom is taken to be invariant in time and to be harmonic in the regions around the lattice site  $r_0$  and  $r_v$ . The curvature of the harmonic potentials is taken to be the same as that deduced for the perfect crystal by analysis of  $\Theta$ ,<sup>4</sup> or of the elastic constants,<sup>5</sup> which is effectively the same assumption. The simple superposition of these harmonic potentials would produce much too large an estimate of  $\Delta H_m$  and a cusped potential along the reaction coordinate, which would seem unphysical. Therefore, this cusp is smoothed off as shown by an assumption of anharmonicity in the GFM. The height of the potential at  $r_s$ , which equals  $\Delta H_m(V)$ , is assumed to be a constant fraction of the simple-harmonic potential, the cusp  $P_{\text{sh}}(r_s)$  for a given crystal structure. In Ref. 5 this constant fraction is denoted as  $\delta^2$  so that

$$\Delta H_m(V) = \delta^2 P_{\text{sh}}(r_s) \quad (9)$$

with  $\delta^2(\text{fcc}) = 0.104$  and  $\delta^2(\text{bcc}) = 0.067$ . These em-

pirically adjusted parameters of the GFM are radically less than those of the BM, Eqs. (7) and (8), and are rather difficult to justify quantitatively. They imply that the time required for the migration event is longer in the GFM than in the BM by about a factor of 3. Thus the GFM event would require about three zone-boundary phonon periods, which seems most unphysical for direct migration in a simple structure. Moreover, the GFM assumes that the potential for small displacements of the mobile atom towards the vacancy is the same as in the perfect crystal. This assumption seems much more dubious than that of the BM, that the tangential modes of the butting atoms are unaffected, and has never been vigorously defended.<sup>4,5</sup> We may terminate this comparison of the GFM and BM by concluding that the reason the two models lead to the same formula is not that they are equivalent but that momentum and position are conjugate variables which enter the harmonic Hamiltonian in the same quadratic form.<sup>20</sup>

Consider now the problem of the anomalous suppression of the low-temperature vacancy migration processes in Si and Ge,<sup>9-13</sup> noted in Fig. 1. One can see in Table I that the calculated BM values  $\Delta H_m(V, \text{Si}) = 1.18$  eV and  $\Delta H_m(V, \text{Ge}) = 1.11$  eV agree with the measured high-temperature values  $1.2 \pm 0.3$  eV,<sup>11</sup> and  $1.0 \pm 0.2$  eV,<sup>12</sup> within experimental accuracy. This does not prove that the high-temperature migration process in these open, covalent structures<sup>13</sup> is ballistic or similar to that illustrated in Fig. 2, but it is clear that the low-temperature process for which  $\Delta H_m(V)$  is an order of magnitude less<sup>9,10</sup>

$$\Delta H_m(V^x, \text{Si}) = 0.33 \text{ eV}, \quad \Delta H_m(V^{-2}, \text{Si}) = 0.18 \text{ eV},$$

$$\Delta H_m(V^x, \text{Ge}) = 0.2 \text{ eV}, \quad \Delta H_m(V^+, \text{Ge}) = 0.1 \text{ eV}$$

cannot possibly be simple direct ballistic migrations. Because these low-temperature values of  $\Delta H_m$  are so small for Si and Ge, the kinetic energy of the mobile atoms in these processes must always be small. The mobile atom cannot move more than about  $\frac{1}{3}$  the distance to a saddle point in the half-period of an optic or zone-boundary phonon that the butting atoms are spread apart before they rebound.

It has been shown<sup>13</sup> that one can account for both sets of values for  $\Delta H_m(V)$  in Si and Ge in terms of the macroscopic cavity model.<sup>21</sup> It was concluded that the low-temperature process involves a correlated (or cooperative) motion of several surrounding atoms so as to attain the minimum activation energy consistent with the necessity to break nearest-neighbor covalent bonds.<sup>13</sup> This correlated motion with its exceptionally low  $\Delta H_m(V)$  is possible because of the directional covalent bonding and open structure of the Si lattice. Similar low-tem-



perature vacancy processes are not expected or observed in noncovalent close-packed structures. They are observed in Si and Ge only at temperatures well below  $\Theta$ , typically around  $\frac{1}{5}\Theta$ , where optic and zone-boundary phonons are not generally excited. At such temperatures the mobile atom can slither along a complex path in configuration space and pass through the very lowest saddle point. However, when optic and zone-boundary phonons are excited, the potential along this complex path is

modulated with the frequency of these phonons and the mobile atoms do not have sufficient time to travel more than a small fraction of the distance to the lowest saddle point before the surrounding atoms rebound and knock the mobile atom back towards  $r_0$ . Thus, raising the crystal temperature above  $\Theta$  suppresses the contribution to  $D_v$  from the low-temperature process by causing the mobile atom to reverse its course several times in its transit from initial to final position.

\*Present address: IBM Thomas J. Watson Research Center, Yorktown Heights N.Y. 10598.

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