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Asymmetry of anion and cation vacancy migration enthalpies in III-V compound semiconductors: Role of the kinetic energy

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In separate publications we have, from a variety of considerations, identified the activation enthalpies for migration by nearest-neighbor hopping, ΔH_m, of vacancies in InP as $\Delta H_m(V_{\rm In})=0.3$ eV and $\Delta H_m(V_{\rm P})=1.2$ eV. These are in the ratio of the masses of the P and In atoms that actually move when $V_{\rm In}$'s and $V_{\rm P}$'s hop to nearest-neighbor sites. Here we argue that this is evidence for the validity of the kinetic interpretation of ΔH_m and the ballistic model of vacancy migration. Indeed, the empirical values are in quantitative agreement with the predictions of the ballistic model. Excellent agreement is also found for $V_{\rm Mg}$ migration in MgO. We extrapolate this result to predict that high-temperature values for interstitial migration in Si and other tetrahedral semiconductors will also be dominated by a kinetic-energy term and far larger than low-temperature values are known to be.

I. INTRODUCTION

A "first-principles" treatment of atomic diffusion must treat $3(N-1)$ atomic coordinates and $3(N-1)$ momenta, where N is the number of atoms in the sample affected by the migration process. Unfortunately, it seems first-principles results are available[1] only for a few highly ionic crystals, such as MgO. This is because the interatomic (interionic) potentials of highly ionic crystals are more easily simulated in a computer than are, e.g., those of crystals with a high degree of directional covalent bonding. Even so, it was necessary to calculate interactions among 64 atoms to obtain convergence[1] for the case of MgO. To date, almost all attempts to deal quantitatively with diffusion processes in semiconductors have invoked major simplifications.

A common approach to the problem of making practical estimates is to neglect the momenta and consider only the potential energy associated with the migration of a particular atom. In this approach the activation enthalpy of migration ΔH_m, for vacancies and for other point defects, is regarded as a purely potential energy; it is then just the potential energy of the configuration at the saddle point of the migration path between the initial and final state of the defect. It is just now becoming feasible to calculate this total potential energy for a configuration at a proposed saddle point in a covalent solid such as Si by Green's-function techniques[2,3] that are self-consistent in the sense that they allow the atoms nearest to the point defect to relax their positions. In addition to the assumption that this range allowed for the defect perturbation is adequate to obtain convergence of the calculated values, most such calculations make the "local-density approximation" for exchange and correlation.[3] The local-density approximation is known to give good (1%) accuracy for properties such as equilibrium lattice constant but poor (factor-of-2) accuracy for band gaps. Thus, one can only speculate at the accuracy obtained for diffusion parameters by the Green's-function method at this time. However, our purpose here is not to discuss the convergence of Green's-function calculations or the adequacy of the local-density approximation or any other nuance of large-scale computer calculations. Instead, we wish to challenge the assumptions: (i) that only potential energies need be considered; and (ii) that values for ΔH_m deduced at very low temperatures T may be assumed to hold also at processing temperatures near the melting point.

While Green's-function treatments are quite new, semiempirical treatments of vacancy migration have been available for several years.[4–6] A particularly simple treatment of vacancy migration in elemental crystals using the purely potential energy approach was presented[4,5] by Glyde and by Flynn. They replaced the $3(N-1)$-dimensional configuration coordinate space by a single reaction coordinate and took the potential energy along this coordinate to be a set of interatomic potentials centered at each lattice site. These atomic potentials were truncated with a parameter fixed for each crystal structure and fitted to the elastic constants of the perfect crystal using the Debye temperature Θ (see Fig. 1). This method gives an excellent fit to empirical values for ten fcc, one hcp, and three bcc elemental crystals.[6] These constituted all cases for which values of $\Delta H_m(V)$ had been established when Ref. 6 was written in 1975. In Ref. 6 one of us (J.A.V.V.) presented an alternative, "ballistic," semiempirical model which, for elemental crystals, gives numerically identical values of ΔH_m, but which supposes a very different physical picture. The ballistic model (BM) also gives values for ΔH_m which are distinctly different from those of the Glyde-Flynn model (GFM) when both are applied to

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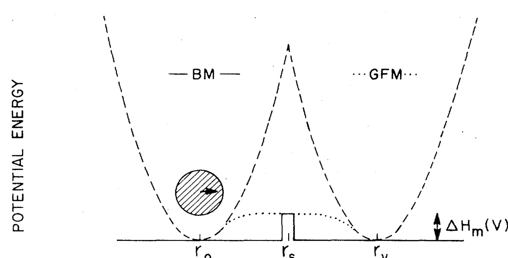

FIG. 1. Potential along migration path: · · · · as assumed in the Glyde-Flynn model, GFM, which is a truncation of an harmonic potential centered on each lattice site and fitted to the Debye potential of the perfect crystal; —— as assumed in the ballistic model, BM, where the potential energy encountered during the average hopping event is assumed to be small compared with the kinetic energy of the migrating atom, except at the saddle point. The two models thus differ fundamentally in regard to the velocity with which the migrating atom is assumed to pass through the broad region around the saddle point; in the GFM it passes much more slowly than in the BM.

atomic diffusion in compounds containing cations that are distinctly heavier than their anions. We now have evidence that, at least for the cases of V_{In} and V_P in InP and for V_{Mg} in MgO, it is the BM that gives the correct result. We shall here discuss this evidence and its implications for the diffusion of interstitial atoms.

An implicit assumption of the GFM is that these single-dimensional contours, that represent the true multidimensional contours, remain constant while the mobile atom moves. Thus, it is assumed that the venue of the migration opportunity is effectively infinite; the moving atom may pass from one step to the next arbitrarily slowly without losing the opportunity to move on the favorable contour on which it began. We note that when $\Delta H_m \gg kT$, the migrating atom is unlikely to have significantly more energy than ΔH_m during the migration event. If an atom starts down the reaction path of the GFM (Fig. 1) with kinetic energy only slightly greater than ΔH_m, then it will slow to a very small velocity while it passes through a broad region about the saddle point. Thus, a relatively long time, many phonon periods, will be required for the migration event if the GFM physical picture is correct. We contend that this assumption is likely permissible at low T, but not at high T. Thus we begin by noting evidence that, at least in Si and Ge, ΔH_m for vacancies is much greater at high T than at low T. Previous evidence of this effect was the original motivation for Ref. 6.

II. HIGH AND LOW T VALUES FOR ΔH_m IN Si AND Ge

Vacancy migration in Si and Ge has been a controversial subject for years.[6–18] Perhaps the reason for this is that radically different results are obtained for ΔH_m in high T diffusion and quenching experiments than in low T electron irradiation and EPR or ir spectroscopic experiments. Using EPR methods at temperatures below $T = 77$ K, Watkins convincingly identified the single vacancy in Si, V_{Si}, that had been introduced by electron irradiation, and determined[8] ΔH_m $(V_{Si}^0) = 0.33$ eV and $\Delta H_m(V_{Si}^{-2}) = 0.18$ eV. For Ge, Whan deduced[9] (to our satisfaction) using electron irradiation and ir spectroscopy that $\Delta H_m(V_{Ge}^0) = 0.2$ eV and $\Delta H_m(V_{Ge}^+) = 0.1$ eV for $T < 25$ K. However, for Ge near its melting point, diffusion and quenching experiments have convincingly demonstrated (Refs. 10—13) $\Delta H_m(V_{Ge}) = 1.0 \pm 0.2$ eV, where V_{Ge} refers to the appropriate average over the thermal distribution of vacancy charge states. (Note that this is an average over activated processes proceeding in parallel; one could not resolve the discrepancy by positting a value of ΔH_m for some charge state of V_{Ge} other than 0 and + that is much larger than 0.2 eV at all T.) For several years, similar, but perhaps less convincing, data has been available[14,15] for Si to show $\Delta H_m(V_{Si}) 1.2 \pm 0.3$ eV.

The high-temperature diffusion of V_{Si} has been clarified substantially in the last few years. A particularly important contribution comes from the laser quenching[16,17] work of Chantre *et al.* With quench rates of order $10^6\,°\mathrm{C/s}$, which are about 10^3 greater than previous work, they have been able to capture the V_{Si}'s that are introduced while the Si is hot in small, easily identified complexes, particularly the "E center," V_{Si}-P_{Si}, and V_{Si}-Al_{Si}. This allowed them to profile the distribution of these complexes using the deep-level transient-spectroscopy (DLTS) technique (see Fig. 2). The profile is peaked at

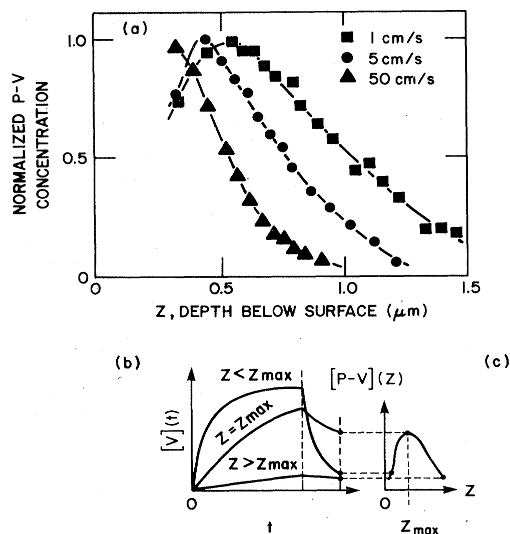

FIG. 2. (a) Distribution of E centers, V-P pairs, in cw-laser-quenched Si for three different laser scanning speeds as determined by Chantre *et al.*, Ref. 16, using the DLTS profiling technique. (Data could not be obtained very near the surface due to limitations of the technique.) Note that E-center concentration decreases near the surface and that the depth of its maximum, Z_{max} is greater for slower scanning rates, which produce the smaller quench rates. (b) Equilibrium concentration of vacancies at three depth as a function of time as calculated by Chantre *et al.* (c) Theoretical distribution of E centers for typical cw-laser-quenching experiment calculated by Chantre *et al.* using high T value of ΔH_m for Si vacancy; compare with 2(a).

depth $z_{\max}$ beneath the surface, because the V_{Si} must first diffuse into the sample from the surface where they are created during the period that it is hot (but not melted), and then tend to migrate back out during the quench phase while the temperature is dropping. Vacancies near the surface at that time are likely to diffuse to the surface. There they are annihilated to reestablish a concentration near thermal equilibrium. The vacancies that have diffused deeper into the sample are less likely to diffuse back out so their concentration becomes greatly supersaturated when T drops; these vacancies then form metastable complexes with dopant atoms. From a proper analysis of this profile[16] one obtains firm evidence that $\Delta H_m(V_{Si}) \approx 1.3$ eV and that the vacancy diffusivity $D_V \approx 4.5 \times 10^{-5}$ cm^2 for $T \sim 1550$ K. If $\Delta H_m(V_{Si})$ were as small as the values determined at low T, then D_V would vary only slowly with T and the concentration of V_{Si} complexes would not decrease rapidly toward the surface. From analysis of the magnitude of the concentration-versus-depth curve, one also deduces[7,16] that the enthalpy of vacancy formation must be about 2.6 eV, which is consistent with early determinations.

Another important advance in understanding high temperature diffusion in Si comes from much improved data for the Si self-diffusion,[18] particularly below 1200 °C. It is now clear that the activation energy for self-diffusion in Si increases with rising temperature; that subject is discussed in Ref. 7.

The distinction between low T and high T values of $\Delta H_m(V)$ in Si and Ge, which was strongly suggested by the data available in 1975, is now firmly established. An explanation for the magnitude of the low T values in terms of empirical values of the directional, covalent part of the total cohesive energy of Si and Ge has been given[19] and need not be repeated here. In order to obtain the low T values of ΔH_m in the GFM, one would have to invoke a truncation parameter much smaller than that found to fit the other elemental crystals. If the same truncation parameter is used for Si and Ge as for the other fcc crystals, then the GFM gives values of ΔH_m in good agreement with the high T determinations, as does the BM.

III. KINETIC ENERGY AND THE BALLISTIC MODEL FOR ATOMIC MIGRATION

One of us (J.A.V.V.) previously proposed[6] to resolve the discrepancy between high- and low-temperature evaluations of $\Delta H_m(V_{Si})$ by treating the high-temperature values as kinetic energies. The ansatz of this "ballistic model" is that the venue for the hopping of an atom from an initial lattice site, or other metastable position, to its next stable, or metastable, site is not in fact infinite. Instead the venue is limited by the motion of the atoms near that atom which moves because such motion will radically modify the potential contours available to the mobile atom; a path which has a small saddle-point potential energy at the instant the mobile atom begins to move along it will be altered so as to present a much higher potential energy barrier before the mobile atom manages to complete the path. This is simply because the nearest-neighbor atoms that control the potential energy along that contour have moved (see Fig. 3). In the simplest case of a closed-packed structure, one of these atoms would simply move into the way of the mobile atom and butt it away with its hard core potential. Referring again to Fig. 1, we suppose that when a mobile atom of mass M begins the migration event with kinetic energy $\frac{1}{2}Mv^2 \gtrsim \Delta H_m$, the potential energy increases that it encounters are negligible except in the immediate vicinity of the saddle point so it travels with essentially the same velocity v throughout the event.

The low T values of ΔH_m for vacancies in Si and Ge are so small that the mobile atom cannot have sufficient kinetic energy to complete the process in a zone-boundary phonon period. (The zone-boundary phonons are those appropriate for this consideration because they produce the greatest relative displacement within the unit cell where the event is to occur.) Yet these low T values are very well established.[8,9] Therefore, we suppose that this kinetic limitation is effective only at temperatures above the Debye temperature (about 40% of the melting temperature of a typical semiconductor) so that zone-boundary phonons are usually excited one or more quantum levels above their ground states. At cryogenic temperatures, where the low values of ΔH_m are deduced,[8,9] these zone-boundary phonons are only infrequently excited so the mobile atom is supposed to have a much longer venue to migrate on a particularly favorable diffusion path. Hence the difference between high- and low-temperature determinations of ΔH_m in Si and Ge that was noted above.[6–19]

In the original BM paper,[6] for the high-temperature diffusion regime it was supposed that venue for the migration event can be approximated as inverse of the empirical Debye frequency, $\nu_D = k\Theta/h$, times a structure-dependent fitting parameter, $F = 0.9$ for fcc and hcp crystal structures and $F = 0.8$ for bcc crystal structures. (This expedient saves the difficulty of defining and

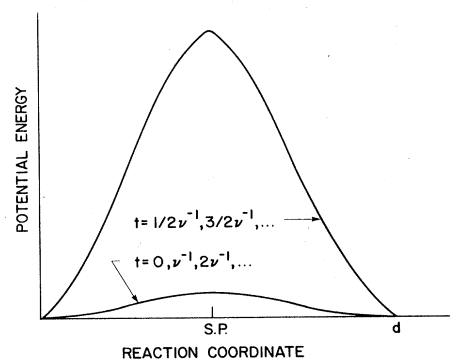

FIG. 3. Potential energy along the path of migration at two instants during the vibration of the surrounding atoms. The large relative displacements of these atoms due to zone-boundary phonon vibrations at high T strongly modulates this potential. Thus, the BM assumes that, for most of the hopping events, the mobile atom begins its migration trajectory when the potential is at its minimum and has passed the saddle point before the potential reaches its maximum, or else it would have been turned back.

evaluating the properly weighted average of the zone-boundary phonons around the surface of the phonon Brillouin zone.) Thus, the formula for ΔH_m is simply

$$\Delta H_m = \tfrac{1}{2} M (F k \Theta d / h)^2 , \quad (1)$$

where d is the distance between the initial and final sites, which is the bond length for the case of nearest-neighbor hopping; we simply take $v = Fd/\nu_D$.

For the elemental crystals the BM gives exactly the same values of ΔH_m, and so the same excellent agreement with available data, as that obtained with the GFM potential energy model, which also used one empirically adjusted fitting parameter per crystal structure and the empirical Θ for each crystal. This agreement in those predictions of the two models should not be interpreted as essential agreement between the models. It is merely a consequence of the symmetry between kinetic and potential energy in the harmonic approximation; the two models differ radically in their assumption of the physical situation, as was noted in Ref. 6. In particular they differ as to how rapidly the mobile atom passes through the region near the saddle point during the most common hopping event and, therefore, as to how the total energy associated with that atom is partitioned between potential energy and kinetic energy.

The BM also takes the attempt frequency ν_0 to be simply ν_D so that the rate of hopping ν at high T is simply

$$\nu = \nu_D \exp(-\Delta H_m / kT) . \quad (2)$$

It might seem that the GFM should assume ν_0 to be much smaller than ν_D because the event would require a time much longer than $1/\nu_D$ to complete in that model. However, it is possible to argue that entropy considerations imply ν_0 should be comparable to ν_D. In fact Flynn suggests[20] $\nu_0/\nu_D = (3/5)^{1/2} = 0.775$ and Sangster and Stoneham found[1] in their computer simulation of V_{Mg} diffusion in MgO that ν_0/ν_D was calculated to be 1.2, i.e., ν_0 was greater than ν_D due to an entropy factor. Unfortunately the empirical value[21] recommended by Sangster and Stoneham for MgO, $\nu_0/\nu_D = 0.9 \pm 0.3$, does not have sufficient precision to make a definitive selection among these three estimates.

The two models differ in respect to their predictions regarding a variation in migration energy with isotope of the diffusing element. The GFM implies almost no difference should be observed between isotopes of the same element because the potential energy at the saddle point (and everywhere else) is independent of isotope. In the approximation that all the kinetic energy is in the migrating atom and none is in the motion of the butting atoms that are vibrating in their zone-boundary mode, the BM implies that the activation energy for a given hop should be proportional to the isotopic mass of the migrating atom. Data for isotope diffusion experiments[22,23] are usually expressed in terms of

$$f \Delta K \equiv (D^a/D^b - 1)/[(m^b/m^a)^{1/2} - 1] , \quad (3)$$

where a and b refer to the two isotopes, m and D denote their respective masses and diffusivities, f is the correlation factor for the mode of migration in question[22] (i.e., the probability the moving atom will not simply go back to its initial position on the next hop), and ΔK indicates the renormalized variation with mass. In the diamond lattice or in the zinc-blende lattice $f = 0.5$ for single vacancy, nearest-neighbor hopping.[22,23] ΔK is assumed to be restricted to the range $0 \leq \Delta K \leq 1.0$. Reported values of ΔK are near 1.0 for fcc metals and near 0.5 for bcc metals. For self-diffusion in Ge at high T, which is likely dominated by single, ionized vacancies,[13,22,23] Campbell reports[23] $\Delta K \sim 0.6$, which is rather less than $\Delta K = 0.86$ that was reported earlier.[22] Because the relation between ΔK and $d\Delta H_m/dm$ is neither direct nor well established,[23] we are reluctant to draw a definitive conclusion from this data. Unfortunately there are only few such isotope diffusion data available for semiconductors.

To distinguish between the GFM and BM experimentally, it would seem the ideal approach would be to obtain empirical values of the various ΔH_m's corresponding to the hopping of different elementals in a compound crystals and then to compare these values to those predicted by the extrapolation of the two models to those compounds. We are now able to do this for the case of V_{Mg} diffusion in MgO using the results of Refs. 1 and 21 and for V_{In} and V_P nearest-neighbor hopping in InP using our own recent results.[24,25]

IV. VACANCY MIGRATION IN COMPOUND CRYSTALS

In an AB compound crystal, where A is the cation and B the anion, a cation or anion vacancy, V_a or V_b, can migrate either by the motion of B atoms or A atoms and may or may not involve the formation of antisite defects, B_a and A_b,[24–27] depending on whether the vacancies hop to nearest neighbors, on the opposite sublattice, or are restricted to their own sublattice. The predictions of the BM for this case are quite obvious and definite. From Eq. (1) we see that for any particular hop ΔH_m is linearly proportional to the mass of the atom that actually does the hop and that it is proportional to the square of the length of the hop d. Moreover, by comparing the extra ΔH_m energy required for a hop that keeps the vacancy on its own sublattice with the calculated value[26] for that required to create an antisite defect by letting the vacancy hop to its nearest neighbor, we can predict which mode is more probable for a given case. As discussed in Ref. 26, the prediction is that nearest-neighbor hopping should predominate in III-V compounds and lattice-restricted, second-neighbor hopping should predominate in most tetrahedral and all rock-salt structure II-VI compounds. The prominence of nearest-neighbor hopping of anion vacancies in III-V compounds has now been established from experimental observation using superlattice structures of host interdiffusion on both sublattices.[24,27,28] In Ref. 24 and in the preceding paper we have given evidence of the importance of nearest-neighbor hopping also for the cation vacancy, at least for the case of InP.

It seems that the extension of the GFM to these same questions regarding compound crystals requires some convention for relating the saddle point potential to some accessible, empirical parameter. It is not clear to us what such an extension of the GFM would predict regarding

first- or second-nearest-neighbor hopping, but it is clear that it does not predict ΔH_m to be linearly proportional to the mass of the atom that actually moves; the kinetic energy is unimportant in the GFM. Instead, we argue that the GFM implies that ΔH_m would always be greater when an anion atom moves than when a cation atom moves because the bond bending force constants are always stiffer for bonds about an anion than about a cation.[29] Consequently, the ideal test cases are AB compounds with $M_A \gg M_B$; then, for nearest-neighbor hopping, the BM predicts

$$\Delta H_m(V_a)/\Delta H_m(V_b)=M_b/M_a \ll 1 , \tag{4}$$

while the GFM predicts the same ratio should be $\gg 1$. One could also make the more simple argument that, since there is only one type of bond in tetrahedral III-V-compound crystal, the A—B bond, $\Delta H_m(V_a)=\Delta H_m(V_b)$ for any A and any B.

InP and MgO satisfy the condition that $M_A \gg M_B$ and we now have empirical values for vacancy migration. In Ref. 24 we found (for nearest-neighbor hopping) that $\Delta H_m(V_P)=1.2$ eV (i.e., In-atom hopping); there and in the preceding paper we found that $\Delta H_m(V_{In})=0.3$ eV (i.e., P-atom hopping). Not only do these values satisfy the ratio given in Eq. (4), but also, as noted before[24] they are in quantitative agreement with Eq. (1). Note that no adjustment of any BM parameter has been made; the same value of the F parameter, $F=0.9$, as has been used was determined using the elemental fcc crystals, including Si and Ge.

One further compound crystal datum we have found to test Eq. (1) is that for V_{Mg} diffusion around 1400 °C, which was analyzed and successfully computer simulated[1] by Sangster and Stoneham. In this case, as expected, the V_{Mg} hops between sites on its own sublattice of its rocksalt (fcc) lattice; it is a Mg ion that does the migration. Therefore, we take M to be the mass of the Mg atom and d to be the spacing between Mg sites, $d=0.2148$ nm at 1400 °C according to Sangster and Stoneham, and $\Theta=941$ K, also according to Ref. 1. Again taking $F=0.9$, as for all other fcc crystals, Eq. (1) gives $\Delta H_m(V_{Mg})=2.27$ eV, which is in good agreement with the empirical value[1,21] 2.3 eV and with the computer simulation value[1] 2.24 eV. As noted above there is also satisfactory agreement as to the value of ν_0; in the most sophisticated version of their computer simulation,[1] Sangster and Stoneham calculated $\nu_0=24\pm1$ THz while they deduce the empirical value to be 18 ± 7 THz. Our value is 19.6 THz while Flynn would suggest[20] 15.2 THz. However, it seems doubtful the GFM could be made to do as well at predicting $\Delta H_m(V_{Mg})$. We do not yet have an empirical value for $\Delta H_m(V_O)$ in MgO to compare with the BM value, 1.49 eV.

V. CONCLUSIONS AND EXTRAPOLATIONS TO INTERSTITIAL MIGRATION

We conclude that the close agreement between Eq. (1) and available data, at least for the good test cases of InP and MgO where the cations are substantially heavier than the anions, is good evidence that the BM is a more realistic approximation than is the GFM of the more probable migration event for vacancies at high temperatures. In particular, ΔH_m for vacancies at high T seems to be determined by kinetic energy, rather than by potential energy, in compounds (where the two assumptions give a different prediction). For the more probable migration events occurring at temperatures above Θ, the migrating atom moves through the broad region around the saddle point in one zone-boundary phonon period or less, rather than in a time much longer than that period.

A consequence of this conclusion is that a calculation of the total energy of the fully relaxed configuration of a proposed saddle-point configuration for the migrating vacancy would not be appropriate for an estimation of ΔH_m at high T; if the fully relaxed configuration were obtained, it would not persist sufficiently long to complete one of the more probable migration events at high T. (However, such a calculation could well be appropriate for low T migration modes.[19])

Furthermore, we propose that our conclusions regarding vacancy migration can be extrapolated to interstitial migration also. The potential energy contour encountered by an interstitial at high T should also be modulated at the frequency of the zone-boundary phonons so that, in the more common migration events, the interstitial will transit between its metastable positions in that period. Such migration will require the corresponding kinetic energy contribution to ΔH_m for interstitials at high T. We expect that this kinetic energy contribution will dominate so that Eq. (1) may also be used to predict high T values of ΔH_m for any host or impurity interstitial; one uses the mass of the interstitial atom, the corresponding d, and the same Θ.

A case of interstitial diffusion of great interest is that for self interstitials in Si.[2,3,7,8,30–32] When these are created by electron irradiation at cryogenic temperatures, they migrate across many lattice sites even at $T=2$ K so rapidly that it has not been possible to measure. The accepted explanation for this rapid, low T migration of the Si self-interstitial is the "Bourgoin-Corbett" athermal mechanism which invokes rapid changes of the ionization state of the interstitial concomitant with the ionization of the sample produced by the electron irradiation that creates the interstitial and a charge state dependent equilibrium position for the interstitial.[32] Recent Green's-function calculations[2,3] support this Bourgoin-Corbett mechanism and its implicit assumption that the differences between relaxed configurations of the interstitial are small compared with the fundamental energy gap, 1.17 eV, indeed of the same order as the low T values of ΔH_m for Si vacancies. The reader should note that the evidence and arguments which have been invoked for a contribution of Si self-interstitials to high T diffusion processes[27,28] require the assumption of a much larger value of ΔH_m for the self-interstitial at high T (see also Ref. 7). Those authors generally posit a value of order 1.5 eV, which indeed corresponds to Eq. (1) with the assumption that the migration step is between the tetrahedral and the hexagonal interstitial sites.

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