

Free Energy and Entropy of Diffusion by *Ab Initio* Molecular Dynamics: Alkali Ions in Silicon

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We have calculated the free energy of diffusion for lithium, sodium, and potassium ions in crystalline silicon by combining a thermodynamical integration method with *ab initio* molecular dynamics simulations. The entropy of diffusion is found to be negative, and its magnitude increases with increasing atomic size of the diffusing species.

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In this paper we demonstrate the feasibility of combining a thermodynamic integration method with *ab initio* total energy calculations in order to evaluate thermodynamic properties. Our particular application of this method is to the diffusion of alkali metal ions in silicon. The diffusion of interstitial impurity atoms in semiconductors is of considerable technological interest [1–8]. Hence it is important to be able to calculate diffusion constants with sufficient accuracy to test the often controversial experimental data [4–8]. A robust simulation method is clearly needed for finite temperature studies of such systems since the use of empirical bonding models is not reliable in simulations of diffusion because the nature of the bonding between the impurity atom and the host material changes radically along the migration path. *Ab initio* electronic structure calculations of the energy barrier height ΔE to diffusion have been carried out in the past using static total energy calculations [9–11]. However, such a calculation cannot give with the same ease a value for the prefactor D_0 in the Arrhenius formula for the diffusion constant

$$D = D_0 \exp(-\Delta E/k_B T). \quad (1)$$

The prefactor D_0 includes the change in the entropy of the lattice vibrations ΔS which arises from the constriction of the diffusing atom when it is at the top of the barrier.

In this Letter we report the first application of thermodynamical integration [12] combined with *ab initio* methods to calculate the entropy of diffusion ΔS (the integration moves the diffusing atom from the bottom to the top of the barrier). The advent of the first principles molecular dynamics (FPMD) method [13–15] allows such calculations to be carried out via a dynamical simulation of the diffusion process with a full quantum mechanical solution of the electronic structure of the system at every time step of the dynamics. The electronic structure problem can be solved either by means of an additional fictitious dynamics of the electrons [13] or by conjugate gradient energy minimization of the electronic subsystem [14]. Such methods give the forces on all the atoms throughout the dynamical simulation, incorporating a full and correct account of the bonding between all the atoms [15]. Our study involves both static evaluations of the energy barrier ΔE and molecular dynamics

based calculations of the free energy of diffusion, $\Delta F = \Delta E - T\Delta S$. We have considered the diffusion of lithium, sodium, and potassium ions in silicon since these species are known to have the same diffusion path in the silicon lattice, namely, along (111) directions in a zigzag fashion [3,16]. We concentrate here on the diffusion of positively charged ions, as experimental data are available for their diffusion constants. In fact, lithium is believed to be present in silicon always in a Li^+ state, while for sodium and potassium both positively charged and neutral states are possible [3].

The preexponential factor can be calculated using the transition-state theory expression [16,17]:

$$D_0 = \frac{1}{2\alpha} \xi g l^2 v^*, \quad v^* = v_0 \exp(\Delta S/k_B), \quad (2)$$

where α is the dimensionality of space, l is the elementary jump length, g is the number of equivalent diffusion paths, and v^* is the attempt frequency. The value of v_0 , the frequency of vibration of the diffusing atom along the diffusion path, is evaluated with all other atoms fixed [2]. The dynamical correction factor ξ accounts for correlated (and reverse) diffusion jumps and is usually set to unity [17], as it is in the present paper.

As already remarked, ΔS arises from the change in vibrational entropy of a real anharmonic solid when the impurity atom moves from its equilibrium position to the saddle point. The physical meaning of ΔS becomes clear from the expression written in the harmonic approximation [17]:

$$\Delta S = k_B \ln \left[\frac{\prod_{i=1}^{3N} v_i^{(0)}}{v_0 \prod_{i=1}^{3N-1} v_i^{(s)}} \right]. \quad (3)$$

Here $v_i^{(0)}$ are the frequencies of the N -atom system (including the diffusing atom) with the diffusing particle in the vicinity of the energy minimum (the particle is not fixed and is allowed to vibrate); $v_i^{(s)}$ are the frequencies of the system with $3N-1$ degrees of freedom where the diffusing particle is at the saddle point and is not allowed to vibrate along the diffusion path. The latter restriction is necessary as the corresponding frequency would be imaginary, so we have to constrain the system in the saddle-point configuration.

It follows from Eq. (3) that the diffusion constant is increased by the entropy contribution if frequencies at the

saddle point are lower than in the equilibrium position. This is the usual situation for vacancy-mediated diffusion, because the diffusing particle feels a softer environment when approaching the vacancy. For the interstitial mechanism the opposite relation between frequencies is expected since the saddle-point configuration is more constricted than the equilibrium ionic arrangement and we expect ΔS to be negative. Moreover we expect $|\Delta S|$ to be small for smaller diffusing species (Li^+ and Na^+ in our case) and larger for the bigger interstitial K^+ . The formulation given in (3) is not very satisfactory for the evaluation of ΔS , because it would involve an evaluation of all the vibrational frequencies of the system with the diffusing atom at the top and the bottom of the barrier. Even then it would represent only an estimate within the harmonic approximation.

Another approach is to evaluate the diffusion constant dynamically from an analysis of the mean squared displacement of the impurity during a molecular dynamics simulation [18,19]. This method allows a determination of the preexponential factor, but it is practical only at temperatures close to the melting point since at lower temperatures diffusion events are too rare to be observed in the molecular dynamics run.

Thermodynamical integration [12] is a practical alternative method for evaluating ΔS . The procedure is to perform molecular dynamics simulations with fixed values of the diffusion coordinate u and evaluate the free energy barrier ΔF as

$$\Delta F = \int_0^1 \langle \partial E / \partial u \rangle_{u,T} du. \quad (4)$$

Here $u=0$ corresponds to the minimum energy state and $u=1$ represents the saddle-point structure. ΔF is the work required to push the diffusing atom from the bottom to the top of the barrier at constant temperature. The requirement of $u=\text{const}$ means that the molecular dynamics run is performed with a constraint, which allows us to evaluate the force tending to push the system down hill. The integral of the statistical average of this force, Eq. (4), gives the amount of work done on the system, which is equal to change in the free energy. For a single inter-

stitial impurity in an infinite crystal $\partial E / \partial u$ is simply the force on the diffusing atom from the rest of the system, suitably scaled because u has been scaled to lie between zero and unity. In a more general situation such as a vacancy (or interstitial in a finite cell with periodic boundary conditions as in the present study) when the diffusion coordinate is a linear combination of the ionic coordinates, the derivative $\partial E / \partial u$ in Eq. (4) can be expressed as a corresponding linear combination of forces. As usual in dynamical simulations the ensemble average in Eq. (4) is taken as a temporal average over the canonical trajectory. The importance of Eq. (4) follows from the fact that it allows ΔF to be calculated as the ensemble average of the derivative of the total energy. In contrast, the free energy itself cannot be obtained by thermal averaging.

We turn now to the details of the calculation. For the electronic structure calculations we used the pseudopotential total energy method [14], employing density-functional theory in the local-density approximation (LDA), Perdew and Zunger's parametrization [20] of the exchange-correlation energy, norm-conserving pseudopotentials of Kerker type [21] in the Kleinman-Bylander form [22], supercells and special points integration over the Brillouin zone, and a plane-wave basis set. We used cubic supercells containing 64 Si atoms and one impurity. The cut-off energy for the plane-wave expansion of the wave functions was 10 Ry. A single $\mathbf{k}$ point (Γ) was used for the Brillouin zone sampling. The effective force $\partial E / \partial u$ in Eq. (4) was derived from the Hellmann-Feynman forces calculated from the electronic structure of the system [14]. For the dynamics the canonical ensemble was simulated using a Nosé thermostat [23]. The ionic equations of motion were integrated using a fifth-order predictor-corrector algorithm with a time step of from 0.2 to 0.5 fs, the total length of the dynamical run being up to 0.4 ps. The conjugate-gradient minimization of the electronic degrees of freedom was repeated after each ionic displacement, and the drift of the constant of motion was maintained to be less than 10^{-3} eV/ionps, which is comparable with the results reported in [15]. At a typical temperature of 1000 K the correction $T\Delta S$ to the energy barrier ΔE is about 0.05 eV for sodium. The

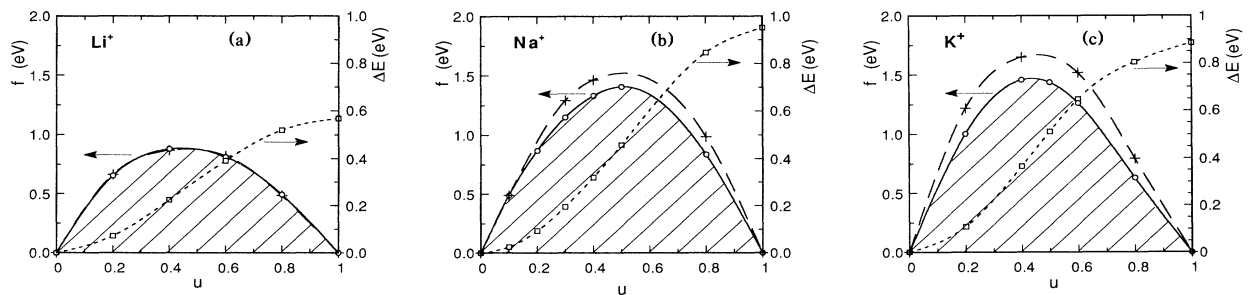


FIG. 1. The shape of the energy barrier for diffusion of Li^+ (a), Na^+ (b), and K^+ (c) in silicon (dotted lines). Solid lines represent the static effective restoring force, and dashed lines correspond to the dynamic average of this force at 1000 K. The scale for forces is given on the left axis, that for ΔE on the right.

error in the values of ΔS comes from averaging over only a few temperatures when using the relationship $\Delta S = (\Delta E - \Delta F)/T$, and from the inaccuracy of the numerical integration of Eq. (4). The ensemble averaging of the effective force introduces a statistical error of approximately 5%. The total error in ΔF is estimated to be of order of 0.01 eV, which gives an accuracy in ΔS of $0.1 k_B$.

We first calculated statically (i.e., at $T=0$) the diffusion pathway and the energy barrier ΔE for Li^+ , K^+ , and Na^+ impurities. In each case the energy minimum was found to occur when the impurity was at the tetrahedral site, and not at the hexagonal site as predicted by Weiser using an empirical bonding description [16]. The hexagonal site is the saddle point for diffusion. The shape of the barrier is shown in Fig. 1 both in terms of the energy and the static force $f_0 = \langle \partial E / \partial u \rangle_{u,T=0}$ along the diffusion trajectory. The accuracy of the numerical integration can be checked by comparing the area of the shaded region (Fig. 1), which is the integral (4) at $T=0$, with the total height ΔE of the barrier. The agreement was found to be better than 5%. Dynamic runs were then performed at a few values of u at different temperatures (from 500 to 1500 K) in the manner described above. The values of $f(u) = \langle \partial E / \partial u \rangle_{u,T}$ are also shown in Fig. 1 for $T=1000$ K. The thermal contribution $-T\Delta S$ to the potential energy barrier is represented by the area between the solid and dashed lines in Fig. 1. Our computed results are reported and compared with experiment in Table I and Fig. 2.

Li^+ is clearly the fastest diffusing species among the elements studied. It has the highest attempt frequency, and the lowest energy barrier for diffusion, which is not decreased by the entropy contribution. The best experimental values quoted for Li^+ in Ref. [3] are $\Delta E = 0.66 \pm 0.01$ eV and $D_0 = (2.5 \pm 0.2) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, although it should be noted that different experimental methods produce quite scattered data [see Table I and Fig. 2(a)]. All in all we regard our results for Li^+ to be in good agreement with the experimental data, and almost certainly more accurate than some.

TABLE I. Results for the interstitial diffusion of positive alkali ions in silicon.

	ν_0 (THz)	ΔE (eV)	ΔS (k_B)	D_0 ($10^{-3} \text{ cm}^2 \text{ s}^{-1}$)
Li^+				
Theory (1000 K)	10.11	0.58	0.0	3.72
Experiment		0.57–0.79 ^a		1.9–9.4 ^a
Na^+				
Theory (500 K)	8.64	0.95	−0.42	2.08
Theory (1000 K)	8.64	0.95	−0.50	1.92
Theory (1500 K)	8.64	0.95	−0.57	1.79
Experiment		0.72 ^b		1.65 ^b
		1.27 ^c		14.7 ^c
K^+				
Theory (1000 K)	9.36	0.89	−1.8	0.59
Experiment		0.76 ^b		1.1 ^b
		0.80 ^d		1.1×10^{-5} ^d

^aReference [3].

^bReference [4].

^cReference [5].

^dReference [6].

For Na^+ we find a small negative ΔS and for K^+ a larger negative value, in accordance with the expected trend. The results for ΔS also follow the size of the static distortion produced in the silicon framework by an impurity ion held at the tetrahedral site, which leads to an increase in the nearest neighbor Si-Si bond length by 0.8% for Li^+ , 2.2% for Na^+ , and 4.5% for K^+ . The calculated values of ΔE and D_0 are also in reasonable agreement with the measurements of Svob [4] who produced the Na and K dopants in an electrically active state using a *p-n* junction technique and probably observed interstitial diffusion, although the value of D might have been overestimated due to trace lithium contamination (see [3]). The only other observation of Na^+ in silicon is due to Doubrava [8] who used the same experimental technique.

Our results for Na^+ and K^+ differ substantially from the other reported experimental values [5–7]. In this connection the following quick estimates are useful. The

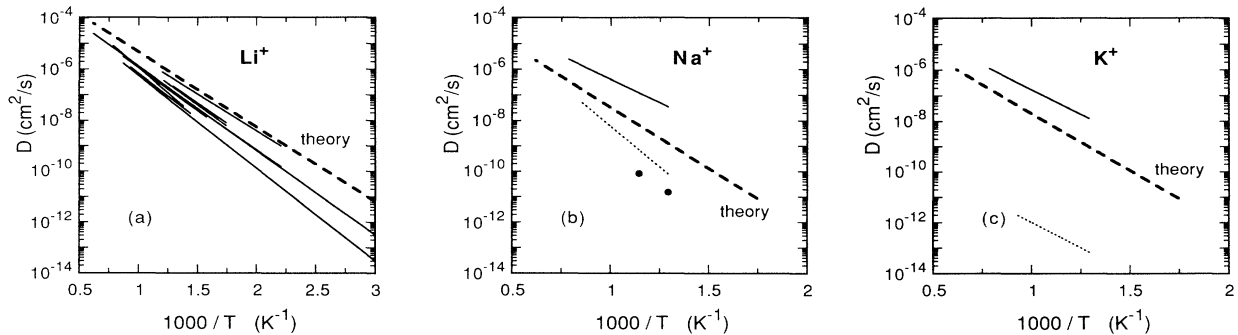


FIG. 2. Theoretical (dashed line) and experimental temperature dependence of the diffusion coefficient for Li^+ (a), Na^+ (b), and K^+ (c) ions in Si: (a) experiment from Ref. [3] (solid lines); (b) experiment from Ref. [4] (solid line), Ref. [5] (dotted line), and Ref. [7] (circles); (c) experiment from Ref. [4] (solid line) and Ref. [6] (dotted line).

frequency of vibration in the minimum energy configuration ν_0 is nearly the same for all three species and is of the order of 10 THz (see Table I), which gives $D_0 = 4 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ where we have used $g=4$ and $\Delta S=0$ in Eq. (2). Thus our results are consistent with the conclusion of Hu [1] in that interstitial diffusion in Si should be characterized by $D_0 \approx 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ and $\Delta E \leq 1 \text{ eV}$. The experimental results of Refs. [5–7] fall considerably outside this range. We suggest therefore that the diffusion constants of sodium and potassium measured in these ion implantation experiments do not correspond to diffusion of positive ions by the interstitial mechanism. The sodium and potassium ions probably prefer to become neutral atoms and become bonded to radiation defects, vacancies, or oxygen impurities. The formation of an impurity-vacancy complex is more likely for potassium, while sodium might become a substitutional impurity as its atomic size is comparable to that of silicon. Note that none of the experimental results for Li [see Fig. 2(a)] was obtained by ion implantation.

In conclusion, we have shown that it is now possible to calculate energy barriers and entropies of diffusion by combining thermodynamical integration [12] with recently developed electronic structure techniques [13,14]. The diffusion of positive alkali ions in silicon is shown to be characterized by a negative migration entropy, and the magnitude of ΔS increases rapidly with increasing atomic size of the impurity. Our calculations represent a major advance because it is difficult to measure diffusion barriers and entropies accurately, particularly if more than one diffusing species or different charge states are present, and previous theoretical calculations have been flawed by inadequate knowledge of the interatomic bonding forces.

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