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Contribution of concerted exchange to the entropy of self-diffusion in Si

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The concerted-exchange (CE) mechanism is at present the only viable candidate for atomic exchange that does not involve intrinsic lattice defects. In order to evaluate its contribution to self-diffusion in Si, we calculate the entropy associated with CE. We include full relaxation of the energy surface through an interatomic potential and take into account the dominant contributions of vibrational modes through the harmonic approximation. This gives an entropy of $6.3k_B$, which accounts for a large portion of the experimental result ($7k_B$–$9k_B$). We conclude that the CE mechanism is a signficant contributor to self-diffusion in Si.

Diffusion is one of the fundamental processes that determines the stability of a solid and its ability to act as host of foreign atoms. In the case of semiconductors the latter property is of crucial importance for doping. Despite decades of intensive study, our understanding of diffusion in Si, the prototypical semiconductor, is still incomplete. In particular, the very high entropy associated with self-diffusion in Si (of order $10k_B$) (Ref. 1) remains somewhat of a puzzle. It has been widely assumed that diffusion mechanisms for Si involve intrinsic defects of the perfect crystal (vacancies and interstitials), which propagate through the lattice with a small activation energy. Direct exchange of atoms was generally dismissed as a viable diffusion mechanism in Si and other covalently bonded solids, due to the high activation energy associated with breaking covalent bonds in the perfect crystal. The proposal of Glazman and Mayaken'kaya[2] that direct exchange of atoms takes place in Si at high temperature had not been accepted as plausible.[1] The only case in which direct exchange was thought to be viable in a covalent solid was that of graphite,[3] due to its low coordination. Even in this case, however, Kaxiras and Pandey showed from first-principles calculations that direct exchange is highly unlikely.[4]

Pandey introduced a mechanism for atomic exchange in Si, which involves concerted motion of a pair of atoms (called concerted exchange—CE) (see Fig. 1).[5] In contrast to direct exchange, which involves a 180° rotation on a single plane, the CE mechanism involves a complicated motion in three-dimensional space which allows the atoms to avoid large energy barriers. This mechanism has an activation energy of 4.3 eV, which is comparable to that of defect mechanisms (3.5–4.5 eV) (Ref. 6) and within the range of experimental values (4–5 eV).[1] Moreover, Pandey and Kaxiras used the energy surface of the *ideal* CE (i.e., neglecting atomic relaxation) to obtain an approximate *lower bound* for the entropy.[7] This lower bound was found to be $3.3k_B$, which is considerably higher than previous estimates of the entropy of defect mechanisms ($\sim 1k_B$),[8] but still lower than experiment ($7k_B$–$9k_B$).[1] Recent first-principles molecular-dynamics simulations by Blöchl, Laks, and Pantelides[9] have found that defect mechanisms can also have entropies comparable to experiment. The issue of the dominant self-diffusion mechanism in Si remains as controversial as it is technologically important.

Since all candidates for self-diffusion in Si have comparable activation energies, accurate calculation of the entropies becomes a crucial issue. Here, we undertake such a calculation for the entropy of CE. This is accomplished by taking into account full atomic relaxation and by enlarging the coordinate space beyond the two angular coordinates that describe the ideal CE path.[5,7] Atomic relaxation is calculated through an effective interatomic

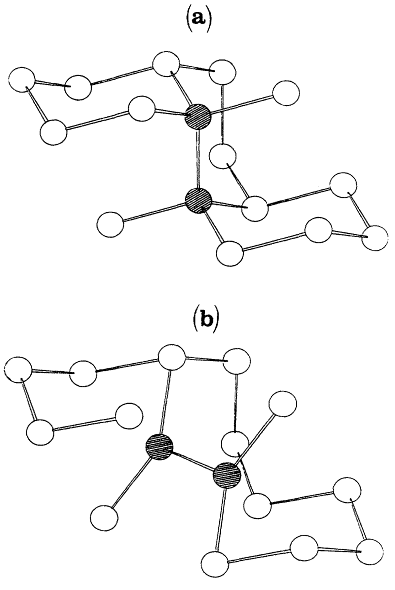

FIG. 1. Perspective view of (a) the equilibrium and (b) the saddle-point configurations for the concerted-exchange mechanism. The exchanging atoms are shown shaded.

potential for Si which was constructed to give an excellent representation of the ideal CE energy surface. The enlarged coordinate space includes the vibration of the exchange-pair atoms relative to one another and their motion as a unit relative to their environment. The contribution of these two modes to the entropy is evaluated through the harmonic approximation. With these extensions we were able to obtain a more accurate estimate for the CE entropy, which is $6.3k_B$. This is reasonably close to experimental results and is still a *lower bound.* We interpret these results as evidence that the CE mechanism is a significant contributor to self-diffusion in Si.

We review briefly the formalism on which the calculations were based. The diffusion constant is given by

$$D = \sum_i f_i a_i^2 \nu_i(T) e^{S_i/k_B} e^{-E_i^a/k_B T}, \tag{1}$$

where the sum runs over all contributing mechanisms, f_i, a_i, ν_i are a geometric factor, the length of each hop, and the attempt frequency, and E_i^a and S_i are the activation energy and the entropy associated with the ith mechanism.[10] For defect mechanisms the concentration also enters in the diffusion constant through the formation free energy. In Vineyard's transition state theory,[11] the entropy is given as the logarithm of the ratio of two integrals

$$S(T) = k_B \ln \left[\frac{I_S(T)}{I_V(T)} \right], \tag{2}$$

where

$$I_S(T) = \int_S e^{-E'/k_B T} dS \tag{3}$$

and

$$I_V(T) = \int_V e^{-E/k_B T} dV \tag{4}$$

with E the total energy measured from the equilibrium configuration and $E' = E - E^a$ the total energy measured from the saddle-point configuration. $dS = ds_1 ds_2 \cdots ds_{3N-1}$ and $dV = dv_1 dv_2 \cdots dv_{3N}$ are the multidimensional regions of integration around the saddle-point and the equilibrium configurations, respectively. The saddle-point integral I_S is over a surface that passes through the saddle-point configuration and is perpendicular to constant-energy contours (the "saddle-point surface"). For all points on this surface, $E' \geq 0$. We have found that the usual harmonic approximation[12] is not adequate for the evaluation of the integral I_S for the ideal CE.[7]

The total-energy surface for the ideal CE was calculated through local-density functional (LDF) theory (for details see Ref. 5). We have constructed an effective two- and three-body interatomic potential[13] which reproduces the equilibrium volume, cohesive energy, and bulk modulus of the diamond lattice for Si, and the LDF results along the path of exchange, *as well as along the path perpendicular to exchange near the saddle-point configuration.* We emphasize this last point, because it is important in the entropy calculation: If one restricts the coordinate space to the two angular variables (θ,ϕ) that describe the ideal CE path,[5] the perpendicular path represents the ideal saddle-point surface needed in Eq. (3) [see Fig. 2(a)]. A crucial test of the validity of the poten-

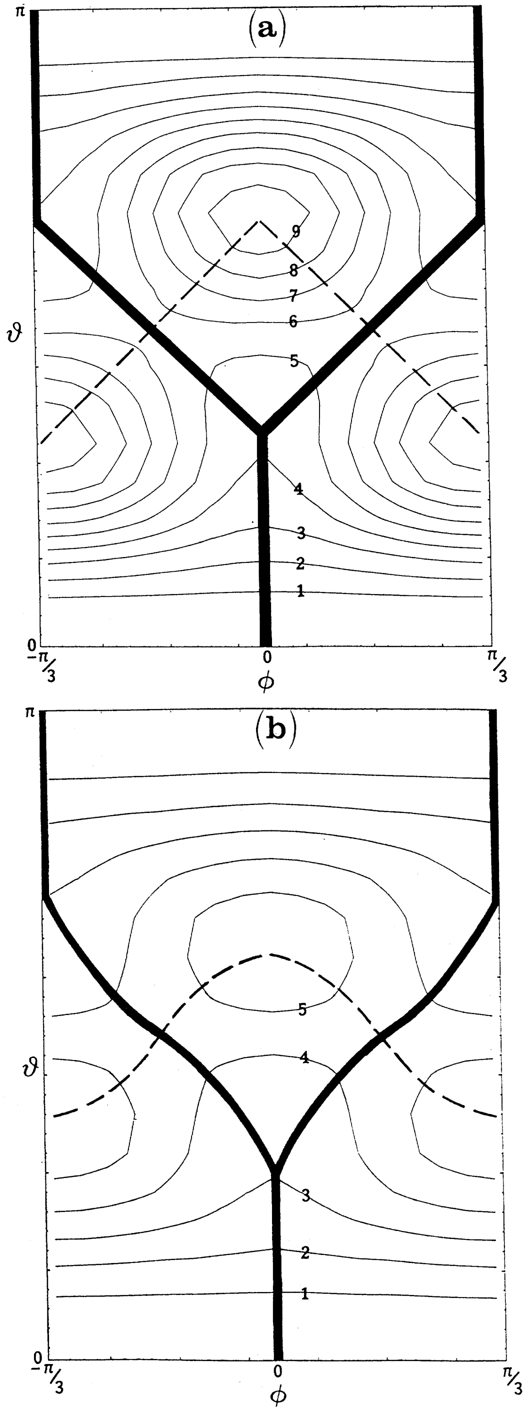

FIG. 2. Total-energy surface for the CE mechanism in the (θ,ϕ) angular coordinates. The contours are labeled in eV. Thick solid lines show the exchange path, dashed lines the saddle-point surface. (a) Unrelaxed energy surface; (b) relaxed energy surface. Note the difference in contour density between (a) and (b), due to a lowering of the energy upon relaxation (contour spacing is the same).

tial is provided by the relaxation of the saddle-point configuration, which has been calculated from first principles in a supercell approximation.[5] Using the same periodic cell as in the LDF calculations (containing 54 Si atoms), we find that our potential gives excellent results for the saddle-point relaxation: the energy gain upon relaxation is 0.7 eV and the bond between the two exchange atoms is shortened by 7% relative to its value in bulk Si. The LDF calculations give exactly the same results in the 54-atom cell. In a larger periodic cell of 128 Si atoms we obtained an additional relaxation energy gain of 0.2 eV. This is consistent with a previous estimate of the long-range relaxation energy based on a Keating model.[5]

Having established that our interatomic potential produces very reasonable results for the saddle-point relaxation, we calculated the entire relaxed energy surface in the (θ, ϕ) coordinate space, through a Monte Carlo procedure using the 128-atom periodic cell. The results are shown in Fig. 2(b). As expected, a considerable lowering of the energy throughout the coordinate space is obtained. The exchange path and saddle-point surface for the ideal CE had been determined from symmetry considerations [see Fig. 2(a) and Ref. 5]. The relaxed exchange path and saddle-point surface can now be *calculated* as the path of steepest descent from the saddle point to the equilibrium configuration, and the surface perpendicular to constant-energy contours that passes through the saddle point, respectively [see Fig. 2(b)]. With this relaxed energy surface, the integrals I_V and I_S in the angular coordinate space can be calculated explicitly without recourse to the harmonic approximation.[7] We have argued before[7] that upon relaxation, the values of both I_V and I_S will increase, but the change in the value of I_S will be much larger than the change in the value of I_V, giving a net increase for the entropy. Indeed, we find that relaxation increases the value of I_S by 73% and the value of I_V by 4%. With these changes the CE entropy takes a value of $5.5k_B$. In Fig. 3 we show the contribution of the CE mechanism to the diffusion constant for the ideal and relaxed calculations. For the present calculation the geometric factor f_i, length of a single hop a_i, and attempt frequency ν_i that enter in the diffusion constant [cf. Eq. (1), with i =CE], are taken to be $f_{CE} = 1$ (see explanation in Ref. 14), $a_{CE} = 2.35$ Å, that is the bond length of Si (the distance by which an atom moves through exchange), and $\nu_{CE} = (\frac{k_BT}{2\pi\mu b^2})^{\frac{1}{2}}$, where $\mu = m_{Si}/2$ is the reduced mass of a pair of Si atoms, and b is their distance at equilibrium ($b = 2.35$ Å).

We consider next the effect of expanding the coordinate space for the relaxed energy surface. We expect each additional degree of freedom to give a positive contribution to the entropy, since for each motion considered the atomic displacements will give a much larger energy gain at the saddle point (where significant relaxation is possible) than at the equilibrium configuration (where little relaxation is possible). Taking into account all the relevant degrees of freedom, and calculating fully relaxed

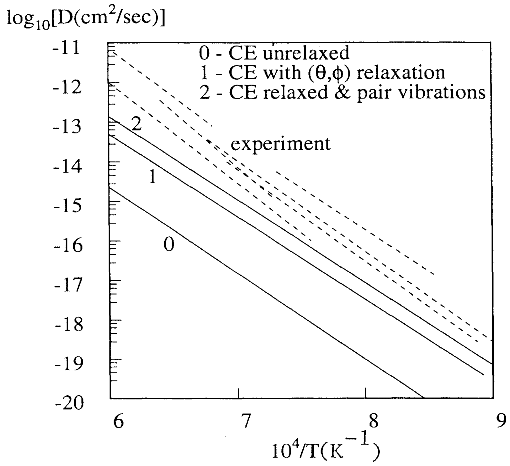

FIG. 3. Diffusion constant for the CE mechanism. Experimental results from Ref. 1 are included (dashed lines). Three stages of the calculation are shown: 0, no relaxation; 1, full relaxation in (θ, ϕ) angular coordinates; 2, full relaxation plus inclusion of two exchange-pair vibrational modes (see text).

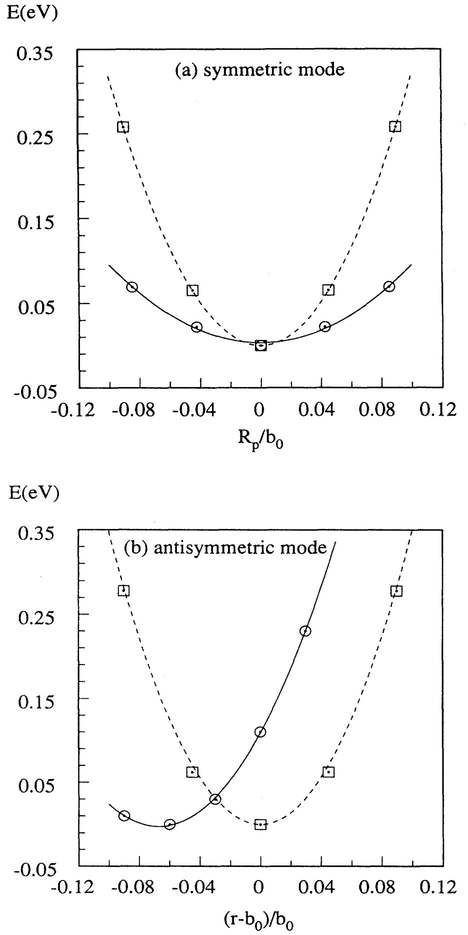

FIG. 4. Energy vs displacement for (a) the symmetric and (b) the antisymmetric vibrational modes of the exchange pair. Dots and squares are calculated values for the saddle point and the equilibrium configurations, respectively. Solid and dashed lines are parabolic fits to the calculations. Displacements are given in terms of relative change from the bulk bond ($b_0 = 2.35$ Å).

energy surfaces is a daunting task, if not an impossible one. Here we discuss only two motions that are easy to visualize, and their contributions to the entropy are easy to calculate. These motions involve the vibration of the two exchange atoms against one another (we call this the antisymmetric mode) and their displacement as a unit relative to their surroundings (which we call the symmetric mode). Intuitively, one expects these two types of motion to give the next most significant contribution to the entropy because they involve degrees of freedom directly related to the highly distorted area of the exchange.

We denote the coordinate of the center of mass of the exchange pair by **R** and the relative distance of the two atoms by r. We assume that the energy changes due to variations in $(\mathbf{R},r)$ and in (θ,ϕ) are independent. This approximation makes the calculation simple, and amounts to neglecting terms in the energy expansion that would couple the two sets of coordinates. We also require the system to remain at the equilibrium and saddle-point configurations as far as the (θ,ϕ) coordinates are concerned while $(\mathbf{R},r)$ are varied. This restricts the possible $(\mathbf{R},r)$ motions along the axis of the exchange pair. We have calculated the energy curves for the symmetric mode (variations in R_p, where R_p is the component of **R** parallel to the exchange-pair axis), and the antisymmetric mode (variations in r). For the equilibrium configuration we use the LDF theory and neglect relaxation, in line with the arguments given above about the role of relaxation. For the saddle-point configuration we use our interatomic potential and include full relaxation in the 128-atom unit cell. The results of these calculations are shown in Fig. 4. The two modes are very nearly harmonic. This justifies the use of the harmonic approximation in evaluating their contribution to the entropy. The stiffness of the symmetric mode is considerably reduced at the saddle point, since in this configuration the exchange pair is connected to only four neighbors, rather than to six as in the equilibrium configuration [compare Figs. 1(a) and 1(b)]. The antisymmetric mode also shows some reduction in stiffness, but not quite as large as the symmetric mode. This is due to the stronger intrapair bond at the saddle-point configuration, which partially compensates for the smaller number of neighbors. The stronger bond at the saddle point comes from π bonding between the two exchanging atoms [note the shorter bond length at the saddle point, which is evident from the position of the energy minima in Fig. 4(b)]. Taking these motions into account gives an increase in the value of the entropy of $0.8k_B$. Our final estimate for the CE entropy is S_{CE}=$6.3k_B$. With this value, the contribution of CE to the diffusion constant accounts for a large portion of the experimentally measured one (see Fig. 3).

In conclusion, we have calculated the contribution of CE to the entropy of self-diffusion in Si, including full relaxation of the energy surface in the space of two angular coordinates that describe the exchange path, and contributions from two vibrational modes of the exchanging atoms. Our final estimate for the entropy is S_{CE}=$6.3k_B$, which lies close to the range of experimental values of $7k_B$–$9k_B$.[1] This estimate is still a lower bound, since, for this particular system, inclusion of more degrees of freedom in the coordinate space will increase the entropy. The reason is that all degrees of freedom in this system have softer modes at the saddle-point configuration, where atoms have either weaker bonds or lower coordination (or both), than in the equilibrium configuration (the ideal crystal) where coordination and bonding is optimal. The only bond that is stronger in the saddle-point configuration is the bond between the exchange atoms themselves. However, even for this bond, the normal mode associated with it is softer at the saddle point than at equilibrium due to the overall coordination of the exchange atoms in the two configurations [see Fig. 4(b)]. Based on these arguments we suggest that the CE mechanism is a significant contributor to self-diffusion in Si, because its entropy of at least $6.3k_B$ accounts for a large portion of the experimentally observed entropy of diffusion (approximately 80% of the *average* experimental value of $8k_B$).

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[1] W. Frank, U. Gösele, H. Mehrer, and A. Seeger, in *Diffusion in Solids II*, edited by A.S. Nowick and G. Murch (Academic, New York, 1985), p. 63.

[2] V.B. Glazman and G.S. Myaken'kaya, Izv. Akad. Nauk Kuz. SSR, Ser. Fiz. Mat. **15**, 28 (1977).

[3] G.J. Dienes, J. Appl. Phys. **23**, 1194 (1952).

[4] E. Kaxiras and K.C. Pandey, Phys. Rev. Lett. **61**, 2693 (1988).

[5] K.C. Pandey, Phys. Rev. Lett. **57**, 2287 (1986).

[6] Y. Bar-Yam and J. Joannopoulos, Phys. Rev. Lett. **52**, 1129 (1984); Phys. Rev. B **30**, 2216 (1984); R. Car, P.J. Kelly, A. Oshiyama, and S.T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984); Phys. Rev. B **30**, 2260 (1984); G.A Baraff and M. Schlüter, *ibid.* **30**, 3460 (1984).

[7] K.C. Pandey and E. Kaxiras, Phys. Rev. Lett. **66**, 915 (1991).

[8] Y. Bar-Yam and J.D. Joannopoulos, in *Microscopic Identification of Electronic Defects in Semiconductors*, edited by N.M. Johnson, S.G. Bishop, and G.D. Watkins, MRS Symposia Proceedings, No. 46 (Materials Research Society, Pittsburgh, PA, 1985).

[9] P.E. Blöchl, D.B. Laks, S.T. Pantelides, E. Smargiarssi, R. Car, W. Andreoni, and M. Parrinello in *Proceedings of 20th International Conference on the Physics of Semiconductors*, edited by E.M. Anastasakis and J.D. Joannopoulos (World Scientific, Singapore, 1990), Vol. 1, p. 533.

[10] W.M. Franklin, in *Diffusion in Solids*, edited by A.S. Nowick and J.J. Burton (Academic, New York, 1975).

[11] G.H. Vineyard, J. Phys. Chem. Solids, **3**, 121 (1957).

[12] G. Jacucci, *Diffusion in Solids II*, edited by A.S. Nowick and G. Murch (Academic, New York, 1985), p. 429.

[13] E. Kaxiras and K.C. Pandey, Phys. Rev. B **38**, 12 376 (1988).

[14] A.D. LeClaire in *Diffusion Processes*, edited by J.N. Sherwood, A.V. Chadwick, W.M. Muir, and F.L. Swinton (Gordon and Breach, London, 1971).