

Free energies of point defects in sodium from first-principles molecular-dynamics simulations

Enrico Smargiassi* and Paul A. Madden

Physical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, England

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The formation free energies of the major point defects in sodium are calculated from first-principles (or *ab initio*) molecular-dynamics simulations, which allow for an accurate representation of the electron density around the defect site. Values are obtained for the vacancy, divacancy, and interstitial for a range of temperatures. The vacancy is found to have the lowest free energy of formation at all temperatures except possibly close to the melting point. Vacancies are found to experience an attractive interaction and may stay bound to each other, to form a divacancy, for a significant period of time. Contrary to previous expectations it is found that at temperatures close to the melting point the interstitial may have a significant presence.

I. INTRODUCTION

The field of defects and self-diffusion in bcc metals has attracted considerable attention in the past 20 years. This is partly due to the anomalous behavior that many of these materials display in the self-diffusion curve at high temperature.¹ At temperatures close to the melting point, the Arrhenius plot of the diffusion coefficient bends upwards, suggesting either a temperature dependence of the diffusion mechanism, or the simultaneous presence of more than one mechanism. Although most of the interest has focused on the technologically important transition metals like Zr or V, the study of simple metals having a bcc structure is important from a conceptual viewpoint. For example, it is also believed that the anomalous diffusion has a common origin with the martensitic transition undergone by many of these materials (in itself an intriguing issue) and in particular that an important contribution to both processes comes from the $\mathbf{q} = (2/3, 2/3, 2/3)$ phonon which is characteristically at very low frequency in the bcc phase. The very simplicity of the electronic structure of simple metals allows one to disentangle geometrical factors from those depending on the electronic structure.¹ In spite of a considerable body of theoretical, numerical, and experimental work, many questions remain unanswered.

Molecular-dynamics (MD) studies of defect properties are a major tool for the study of dynamical properties of matter. In the past, MD studies on simple metals have been conducted using pair potentials (notably of the Dagens-Rasolt type²⁻⁴), which, however, are not completely reliable for defect properties. For example, the activation energy for vacancy-induced self-diffusion in Na was given³ quite correctly as 0.37 eV, but this was a result of a cancellation of errors between a formation energy too low by 30% (0.25 eV vs 0.35 eV) and an activation energy 4 times too large (0.12 eV vs 0.03 eV). It has been argued⁵ that the agreement between the calculated activation energies and the experimental ones (which is found also in Al) is not accidental, but is a consequence

of a systematic cancellation between many-body forces during the process of creating and subsequently moving the defect. However, the exactness of the separate formation and migration energies is of importance. First, the density of defects, a function of the formation free energy, is important in itself. Second, an incorrect migration energy may lead to spurious predictions, and it is difficult to separate these from the genuine ones. Unexpected phenomena have been suggested by a few calculations^{3,4} and, in the case of Ref. 3, not been confirmed experimentally.⁶

The atomic environment around a defect is very different from the bulk and thus a successful description of a defect requires a tailor-made potential. This new potential, however, is likely to be inadequate for the description of bulk properties, like phonons (see the discussion in Ref. 5); this in turn affects the accuracy of the calculation of the free energy of formation of the defect. In other words, in calculations on point defects the transferability problems that affect classical potentials are highlighted. A consistent description of all the defect properties seems to require some sort of explicit treatment of the electronic degrees of freedom.

Nowadays, *ab initio* techniques like the Car-Parrinello method⁷ are available, which explicitly and self-consistently deal with the electronic side of the problem, hence avoiding these difficulties. Application of these "exact" schemes to metals (especially in the solid phase) on the other hand has been held back by their extremely large computational requirements. For example, in a single-particle, Kohn-Sham (KS) representation, reasonable results for simple metals can only be obtained by using a k -point sampling of the Brillouin zone corresponding to at least 30 points in the irreducible zone.⁸ A reasonable description of a point defect, however, requires typically 50 atoms, which means that more than 100 000 plane waves must be used. Moreover, meaningful thermal averaging can be done, as we shall see, only on molecular-dynamics runs about 5 or 6 ps long. This effectively rules out any finite temperature simulation of the KS type on the computers now available.

In this paper, we will illustrate the results of a first-

principles MD study of defect energies and free energies of defects in Na. We used a numerical scheme which gives a first-principles, self-consistent description of alkali metals at the same level of accuracy, but at a fraction of the computational cost, of conventional KS schemes. Rather than use a representation of the kinetic energy functional via the introduction of orbitals (as in the Kohn-Sham representation) we use an explicit functional of the density. In the case of Na we find that the differences between our method, the conventional KS method, and the experiment are very small and probably lie within the basic uncertainties introduced by the local density approximation plus pseudopotential scheme. The major advantage of the orbital-free scheme is that we can easily use cells containing up to 250 atoms (more than 400 for static calculations) and run dynamics for 100 ps if needed.⁹ This makes our method ideally suited for defect calculations in alkali metals.

The method has been described in detail elsewhere,¹⁰ and so has the method of calculation of free energies.¹¹ In this paper we will only show and discuss the results for the major point defects: the vacancy, the divacancy, and the interstitial. There are in fact several different divacancies to be studied; it makes a difference if the two vacant sites are first neighbors, second neighbors, etc. We will call D_n a divacancy in which the vacant sites are n th neighbors. We studied the cases $n = 1 - 4$, as they are probably the most relevant in the diffusion and related processes. Moreover, larger values of n imply a substantial computational effort (due to the need for larger cells) and would give results not much different from the case of a couple of isolated vacancies. As always, the ground-state structure of the interstitial is not *a priori* obvious. We performed an explicit study to find the lowest-energy atomic configurations.

In Sec. II we present the static results regarding formation energies at the absolute zero and the corresponding electronic and ionic structures for all the defects. This enables us to assess the validity of our choice by making systematic comparisons with state-of-the-art KS calculations.⁸ Section III contains the results for the free energies and a discussion of the results. Our conclusions are in Sec. IV.

II. ENERGETICS OF DEFECT FORMATION

A. Preamble

We wish first to compare the prediction of our model for the $T = 0$ energetics of defects in Na with those of a recent accurate study within the KS scheme.⁸ In this way we can check the adequacy of the approximations made in constructing our energy functional and appropriately choose the convergence parameters. Moreover, as we are able to use much larger cells than used in the KS calculations,⁸ we may check for the absence of size effects.

Once the energy functional has been selected, one is left with three main approximations (more details on both

the formalism and the parameters used can be found in Ref. 11). First, one has to choose a suitable pseudopotential to describe the electron-ion interaction. We have chosen a Topp-Hopfield pseudopotential¹² which gives a good description of sodium in a wide variety of circumstances. Second, a plane-wave cutoff must be imposed in order to have a finite number of electronic degrees of freedom. We have found that a cutoff corresponding to a plane-wave energy of about 9 Ry is sufficient for all our purposes. Third, the size of the simulation cell is of importance. An isolated defect will be properly simulated only if the cell is large enough to make the interaction with the periodic images negligible. To be sure that this is the case a separate study for each kind of defect considered is required, especially when ionic relaxation is allowed. In all of what follows, we consider an energy converged if its estimated error is less than 0.01 eV, unless otherwise stated. It is doubtful that a pseudopotential plus local density approximation (LDA) scheme can give more accuracy than this.

A formation (free) energy is calculated as the difference between the energy of a system with the defect and the one of the perfect crystal, at constant number of particles. Of course, the energy functional used and the convergence level must be the same in both cases. There are, however, several possible different choices for the cell volumes. For the perfect crystal, we used the experimental lattice parameters at all temperatures (except at $T = 100$ K where we used the same as $T = 0$), which is the most common and sensible choice. Because of the use of the LDA and the choice of pseudopotential, our scheme overestimates the lattice parameter of Na by 2%; this means that the system is under slight pressure, which we verified is always less than 7 kbar at any temperature.

Once the lattice parameter for the perfect crystal has been chosen, one has to decide the value appropriate for the defective crystal. A “constant lattice parameter” calculation is one which keeps the cell volume equal to that of the perfect crystal. The unrelaxed calculations of Ref. 8 are of this kind. We choose to perform “constant atomic volume” calculations instead, i.e., to scale the volume with the number of atoms actually present in the cell. One might improve by allowing the volume of the cell to relax until the pressure is equal to the pressure experienced by the perfect crystal to which it is compared; this would allow one to calculate the formation volume of the vacancy. In Ref. 8, however, it was found that in sodium the change in energy caused by this relaxation is negligible, and our results confirm this: The pressure difference between the perfect crystal and the defective crystals with constant atomic volume never exceeds 0.5 kbar, suggesting very little change in the energy upon volume relaxation.

B. Vacancy and divacancy

For an isolated vacancy with fixed ions, we found that the formation energy E_V is already converged at a cell size of 16 atoms. Similar conclusions were reached by

TABLE I. Formation energy of the vacancy and divacancy at $T = 0$, including ionic relaxation (unrelaxed energies in brackets). For the vacancy, the KS representation gives 0.36 eV (Ref. 8); the experiments 0.35 eV (Ref. 14).

N	54	128	250
vacancy	0.37 (0.51)	0.37 (0.52)	0.35 (0.51)
D_1	0.81 (1.04)	0.80 (1.04)	0.78 (1.03)
D_2	0.66 (1.00)	0.66 (1.00)	0.65 (0.99)
D_3	0.75 (1.04)	0.76 (1.03)	0.74 (1.03)
D_4	0.69 (1.03)	0.70 (1.04)	0.67 (1.03)

Frank and co-workers^{8,13} in their studies of lithium and sodium. The increase in the cell size therefore brings changes in the total energy only via ionic relaxation. Even so, a 54-atom cell was found to give convergence for the vacancy and all the divacancies, as seen in Table I. We feel that most of the small variations that the energies show at increasing N are due to numerical effects rather than physical changes with the cell. The results agree very well with the available experimental¹⁴ and theoretical⁸ results.

In Fig. 1 we show the magnitude of the relaxation of the first shells of neighbors of the vacancy for two cell sizes (54 and 128 atoms per cell). The relaxation turns out to be symmetric around the vacancy, except for some of the shells which are incompletely included in the cell. However, whenever the cell is enlarged so as to include the full shells the asymmetric part of the relaxation disappears. The asymmetric part of the relaxation is therefore a finite-size effect and it has been excluded from Fig. 1. Again, we see that the convergence is good with a 54-atom cell. The results are also within a few percent of the Kohn-Sham results of Ref. 8.

In Fig. 2 we show the electron density around D_1 . The spherical “holes” in the electron density are an artifact due to the use of a pseudopotential to represent the electron-ion interaction. The bacteriumlike hole in the center is instead real and it corresponds to the alteration in the electronic density due to the presence of the divacancy.

C. Interstitial

Close-packed solids like metals usually do not allow the interstitial to exist in a pure form (by pure we mean an

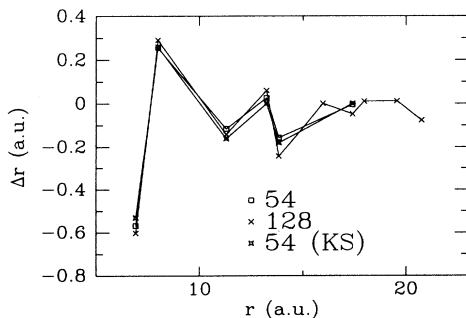


FIG. 1. Relaxation of the ionic shells around the vacancy. Squares: 54-atom cell. Crosses: 128-atom cell. Open crosses: KS results (Ref. 8). The lines are guides for the eye.

atom sitting in an interstice of the crystal, while the others sit in a recognizable distortion of the perfect lattice). Indeed, this is not the case even for several tetrahedrally coordinated materials, whose structure leaves much more room. Instead, it usually happens that an atom close to the interstitial is pushed away from its perfect lattice position. The defect thus is best described as a pair of atoms occupying a single lattice site, with the other atoms still quite close to their original sites. This kind of defect is called a “dumbbell” and it might be thought as a molecule embedded in a crystal. As such, the bond length of the pair may be expected to be of the order of the bond length of the molecule *in vacuo* (5.8 a.u. for Na). A dumbbell is characterized by the direction of the bond between the atoms in question. In a cubic crystal one typically considers the (100), (110), and (111) dumbbells. However, other kinds of interstitial configurations cannot be discarded *a priori*.

We studied the three dumbbells mentioned above, plus two configurations in which a pure interstitial was either in a tetrahedral or an octahedral site. In all cases all atoms were allowed to relax using a steepest-descent procedure until convergence in the energies (an estimated error of less than 10^{-4} hartree) was reached. As already found in other studies,⁸ we found that the change in energy between the initial, unrelaxed configuration and the final one is massive (as large as 2 or 3 eV), in fact much greater than the relaxed formation energy itself. This shows that the “unrelaxed” structures of the interstitial are unphysical and the convergence has to be studied

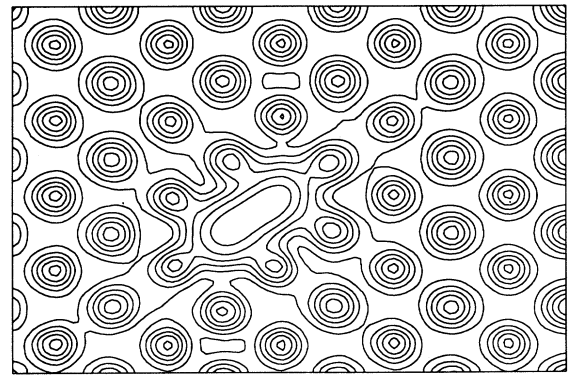


FIG. 2. Electron density around a D_1 divacancy, in a 250-atom cell. The slice is taken along the (110) direction.

on the relaxed energies directly. From Table II we argue that, due to the small differences in energy between some of the competing structures, a 128-atom cell is advisable, although a 54-atom cell is probably sufficiently large for many purposes.

Our values for the formation energies agree well with the KS results of Ref. 8, although ours look systematically lower. We think that at least part of the difference may be explained by a different degree of convergence in the ionic relaxation: As we showed, the ionic relaxation energy is very large and a slightly imperfect convergence may cause sizable errors. Indeed, these are almost to be expected if the relaxation is performed by moving the atoms “by hand.”

As Table II shows, when a 54-atom cell is used, the (110) and (111) dumbbells turn out to be energetically almost equivalent. The bond length between the two atoms is similar too: 5.78 and 5.74 a.u., respectively [to be compared with KS results of 5.51 and 5.47 a.u. (Ref. 8)]. However, when a 128-atom cell is used the (111) configuration becomes somewhat lower in energy [the bond length increases to 5.83 a.u.; that of the (110) dumbbell remains almost the same]. Whether this is significant or not remains to be seen: A change of about 0.02 eV in the formation energies as the cell becomes larger may be expected. Moreover, with such a small energy difference it is almost certain that at finite temperature the two forms are both present simultaneously.

In order to check that no other configuration can have a lower energy than those studied above, we used simulated annealing. We put the extra atom in a tetrahedral site, heated the system to 1500 K, and cooled it down gradually ($\Delta T/T \approx 0.01/\text{step}$) until the instantaneous temperature was of the order of 1 K; then it was quenched until converged. At the end of the run it was found that the atoms forming the dumbbell did not include the original interstitial, which shows that the system had lost memory of the original configuration. In the 54-atom cell we found that the ground state was a (110) dumbbell (bond length 5.79 a.u.), with a formation energy almost equal to that given by the relaxation study. Of course the annealing cannot be expected to discriminate between this structure and the almost degenerate (111) dumbbell. In a 128-atom cell the ground-state configuration was found to be the (111) dumbbell, again with the same formation energy of the relaxation study. We conclude that the static calculations are indeed sufficient to study the ground state of the interstitial.

The electron density along a (100) slice of the crystal crossing a (111) dumbbell is shown in Fig. 3. The

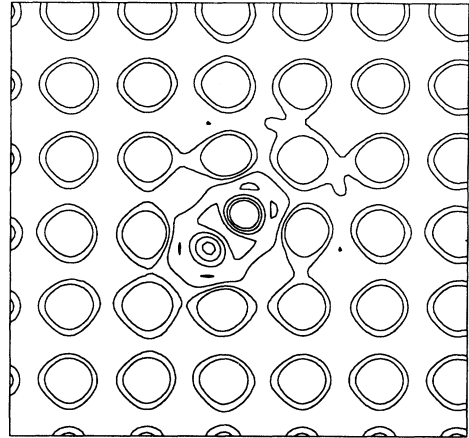


FIG. 3. Electron density around a (111) dumbbell, in a 432-atom cell (see text).

contours corresponding to regions with the lowest electronic density have been omitted, as they only appear in the pseudopotential core region (where the calculated density is unphysical anyway) and would only confuse the figure. The slice crosses the dumbbell approximately midway between the two atoms in question, the rightmost atom being slightly higher than the plane of the figure and the leftmost slightly lower. The buildup of charge between the atoms is clearly reminiscent of the chemical bond in a diatomic molecule; however, there are differences. In particular the pockets of electrons on the outside of the dumbbell appear to be an effect of the crystalline environment. It is interesting to note that in spite of the importance of the ionic relaxation in determining the interstitial formation energy, the distortion of the surrounding lattice is almost undetectable to the naked eye.

III. FREE ENERGIES

A. Preliminaries

1. Defect configurations

As discussed in Ref. 11, for a defect which can exist in m equivalent orientations it is convenient to calculate its

TABLE II. Formation energy of the interstitial at $T = 0$, in eV. Rightmost column: KS data (Ref. 8), obtained using $N = 54$. Full ionic relaxation is allowed.

N	54	128	250	54 (KS)
(100)	0.67	0.66		0.73
(110)	0.55	0.55		0.59
(111)	0.55	0.52	0.50	0.60
oct	0.67	0.66		
tet	0.59	0.59		
annealed	0.55	0.52		

free energy when in a specific form, and then add a term which we call "orientational entropy." This term is given by $S^{\text{or}} = k_B \ln m$ and all one needs to do is to count the number of equivalent configurations.

The vacancy is fully specified by the site in which it sits; hence $m = 1$ and $S^{\text{or}} = 0$. The divacancy D_1 is specified first by the lattice site of one of the pair of vacant sites [let us suppose it is $(0, 0, 0)$]; then, once the first site is fixed there are eight possibilities for finding the second, as it must lie at a lattice site $a(\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2})$ (a is the lattice parameter). However, only half of these must be counted, due to the indistinguishability of the vacancies. Therefore for D_1 , $m = 4$ and $S^{\text{or}} \simeq 1.4$. For the divacancy D_2 , the second vacant site is $a(\pm 1, 0, 0)$ plus all the permutations of axes, giving $m = 6/2 = 3$ and $S^{\text{or}} \simeq 1.1k_B$. For the divacancy D_3 , one has $a(\pm 1, \pm 1, 0)$ (plus permutations), and so $m = 12/2 = 6$ and $S^{\text{or}} \simeq 1.8k_B$. Finally, for D_4 , one has $a(\pm\frac{3}{2}, \pm\frac{1}{2}, \pm\frac{1}{2})$ and $m = 24/2 = 12$ and $S^{\text{or}} \simeq 2.5k_B$.

In principle, all the possible configurations of the interstitial should be studied. We have seen from the energetic considerations that only two of them can be of importance, the (110) and (111) dumbbells. To simplify matters, we decided to take the (111) dumbbell as representative of both. In this case, we consider the (110) and (111) dumbbells to be equivalent; hence $m = 6 + 4 = 10$ and $S^{\text{or}} \simeq 2.3k_B$.

2. λ integration

The technique for calculating the formation free energy F_f^N of a defect has been described in detail in Ref. 11. We summarize here quickly the relevant formulas for the vacancy and the divacancy and derive those for the interstitial. For a vacancy or a divacancy in an N -site cell,

$$F_f^N = - \int_0^1 d\lambda \langle \Phi^N(\lambda) \rangle_{\Omega} + L\Omega_a \int_0^1 d\lambda P(\lambda) + L\Delta F, \quad (1)$$

where $\Phi^N = \frac{\partial U^N}{\partial \lambda}|_{\Omega}$, Ω_a the atomic volume, P is the thermodynamical pressure exerted by the system, and L is the number of atoms to be decoupled to form the defect in question; i.e., $L=1$ for the vacancy and $L=2$ for the divacancy. The cell volume Ω is taken to be a linear function of λ . The potential function $U^N = U^N(\lambda)$ is parametrized so that $U^N(\lambda = 1) = U^N$ is the ionic potential of the perfect crystal, and $U^N(\lambda = 0) = U^N$ is the ionic potential of the crystal with a vacancy or divacancy plus the potential energy of L atoms decoupled from the others and put in L harmonic wells u . These wells are centered in the vacant sites and switched off as λ approaches 1. The oscillation frequency of an atom in u is chosen to be the Debye frequency for sodium: $\omega_D \approx 4.75 \times 10^{-4}$ a.u., ΔF is the difference between the free energy per atom in the perfect crystal and the free energy of an atom in a harmonic well, at the same temperature: $\Delta F = \frac{1}{N} F_C^N - \varphi$, where φ is the free energy of an atom acted

upon by u . The values of ΔF at various temperatures have been calculated previously and published in Ref. 11.

The case of the interstitial is analogous. In this case, however, the defect is best described as two atoms (the dumbbell) gradually appearing in place of a regular lattice atom, as λ approaches 1. The simplest approach is then to take the vacancy crystal and not the perfect crystal as the reference state. In this case, the atoms appear in the site of the vacancy, and

$$U^{N+1}(\lambda = 1) = U_I^{N+1} \quad (2)$$

and

$$U^{N+1}(\lambda = 0) = U_V^{N-1} + 2u, \quad (3)$$

where U_I and U_V refer to the potential energy of the interstitial crystal, and a vacancy crystal, respectively. We then have

$$\begin{aligned} \int_0^1 \frac{\partial F^{N+1}}{\partial \lambda} d\lambda &= F^{N+1}(\lambda = 1) - F^{N+1}(\lambda = 0) \\ &= F_I^{N+1} - F_V^{N-1} - 2\varphi. \end{aligned} \quad (4)$$

In this case, the formation free energy of the interstitial F_{fI}^N is calculated relative to that of the vacancy F_{fV}^N and Eq. (1) has to be suitably modified. By definition,

$$F_{fI}^N = F_I^{N+1} - \frac{N+1}{N} F_C^N = F_I^{N+1} - F_C^N - \frac{F_C^N}{N} \quad (5)$$

and

$$F_{fV}^N = F_V^{N-1} - \frac{N-1}{N} F_C^N = F_V^{N-1} - F_C^N + \frac{F_C^N}{N}. \quad (6)$$

Subtracting Eq. (6) from Eq. (5) we have, in analogy with Eq. (1),¹¹

$$F_{fI}^N = F_{fV}^N + \int_0^1 d\lambda \langle \Phi(\lambda) \rangle_{\Omega} - L\Omega_a \int_0^1 d\lambda P(\lambda) - L\Delta F, \quad (7)$$

with $L=2$.

In the case of the interstitial it is not obvious *a priori* where the dumbbell should appear, i.e., where the harmonic wells u have their center. Considerations of consistency with the $T = 0$ results show that they must be centered at the place where the dumbbell is found to sit in a static calculation after full relaxation of the crystal.

A further set of parameters of importance for the free-energy calculations is then the set of λ points used for the calculation of the integrals above. We checked that two Gauss-Legendre points ($\lambda_1^2 = 0.2113248654$ and $\lambda_2^2 = 1 - \lambda_1^2 = 0.7886751346$, both with weight $1/2$) are sufficient to give convergence for the vacancy and all the divacancies. The interstitial, however, causes a much larger ionic relaxation and this requires the use of three points: $\lambda_1^3 = 0.1127016654$, $\lambda_2^3 = 1 - \lambda_1^3 = 0.8872983346$, both with weight $5/18$, and $\lambda_3^3 = 0.5$, with weight $8/18$. The integrals over the pressure gave the desired convergence

with just one or (for the interstitial) two λ points.

The molecular-dynamics run lengths were chosen to be about 6 ps, including thermalization. To check that this is sufficient for the desired statistical convergence, after each run we calculated the averages by discarding sections of different length from the beginning of the run. We found that discarding the first 2 or 4 ps (i.e., retaining 4 or 2 ps for thermal averaging, respectively) leads to results very similar to each other. However, discarding 1 or 5 ps leads to significant differences. Allowing 2 ps of thermalization and 2 ps for thermal averaging therefore seems necessary and sufficient. Test runs as long as 12 ps did not change this conclusion.

B. Results

1. Vacancy and divacancies

The free energy of formation $F_{fV} - TS_V^{or}$ of the vacancy is shown in Fig. 4, as a function of the temperature. Although from the slope of the curve it is in principle possible to calculate the formation entropy, in practice the statistical uncertainty prevents this, even if more T points had been calculated. All that can be said is that S_f is of order $1k_B$ or $2k_B$ at low temperature and probably increases to about $4k_B$ or $5k_B$ in the vicinity of the melting point. One conspicuous characteristic of Fig. 4, repeated in almost all the calculations, is the increase in the statistical fluctuation of the results at $T = 370$ K, and the bending downwards of the $F(T)$ curve, indicating a definite increase in entropy. We interpret this as a sign that melting is approaching (370 K is the experimental melting temperature of sodium). Work is in progress to locate the melting point within our model.

Figure 5 shows our results for the various forms of the divacancy. Again the fluctuations increase sharply at 370 K. The formation entropies are $(4-6)k_B$ at low temperatures, and increase probably to about $8k_B$ close to the melting point. The energy differences between the various forms of the divacancy are small but, in our opinion, significant. In particular, the conclusion that D_2 and D_4 are the forms with lowest free energy is in agreement with the experimental findings of Ref. 6.

2. Interaction between vacancies

We may regard a point defect as a kind of quasiparticle, dressed by a cloud of virtual phonons (the ionic relaxation), somewhat analogous to a polaron in an ionic crystal. The defects can interact with each other via the

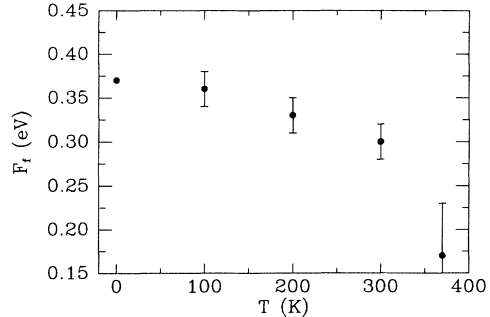


FIG. 4. Formation free energy of the vacancy, in eV (including S^{or}). The error bars show the statistical uncertainty of the results, estimated by the spread in results obtained by starting the statistical averaging at different times along the run.

lattice and with line and surface defects, and can annihilate themselves by recombining with another defect or with a surface. An interesting point to study is whether two vacancies repel or attract, or, equivalently, whether the divacancy is bound or not. In this picture the role of the interaction potential is played by the difference $F_{int} = F_{fn} - 2F_{fV}$. The orientational entropy plays the role of the quasiparticle entropy. To see this, one may just write the equation for the number concentration c_n of two n th neighbor vacancies in the case of $F_{int} = 0$:

$$c_n = e^{(TS^{or} - F_{fn})/k_B T} = m e^{-2F_{fV}/k_B T} = m c_V^2, \quad (8)$$

where m is the number of possible ways in which two n th neighbor vacancies can be found. Therefore, $m = e^{S^{or}/k_B}$ is the configuration space available to the motion of the two vacancies.

The results for F_{int} are shown in Table III. The comparatively large size of the various uncertainties with respect to these values makes any quantitative conclusion dubious; in particular, the results at 370 K are probably unreliable and are not shown. We believe, however, that the qualitative picture is quite clear: At all temperatures there exists at least one divacancy configuration which is stable with respect to dissociation into a pair of separate vacancies. This implies that vacancies in sodium tend to lump together. The small concentration, however (about 10^{-5} per site at 300 K), means that there is much more phase space volume available for isolated vacancies than for bound ones and at equilibrium it is likely that the isolated vacancies outnumber the divacancies.

At large distances the vacancies do not interact; hence we must have $\lim_{n \rightarrow \infty} F_{fn} = 2F_{fV}$. This limit is al-

TABLE III. Interaction free energy F_{int} of two vacancies (eV).

T (K)	0	100	200	300
D_1	0.06	0.04	0.04	0.00
D_2	-0.08	-0.10	-0.14	-0.11
D_3	0.02	0.02	0.01	-0.02
D_4	-0.04	-0.05	-0.04	-0.02

ready reached for $n = 3$ in the static calculations if the ionic relaxation is not allowed, in agreement with the findings of the convergence study for the single vacancy. The difference between F_3 and F_4 is thus entirely due to the ionic relaxation, and so it is the interaction between two well-separated vacancies. The data in Tables I and III suggest that the interaction between two vacancies is nonmonotonic, oscillating around zero, and becomes negligible only when they are as far apart as to be sixth or seventh neighbors.

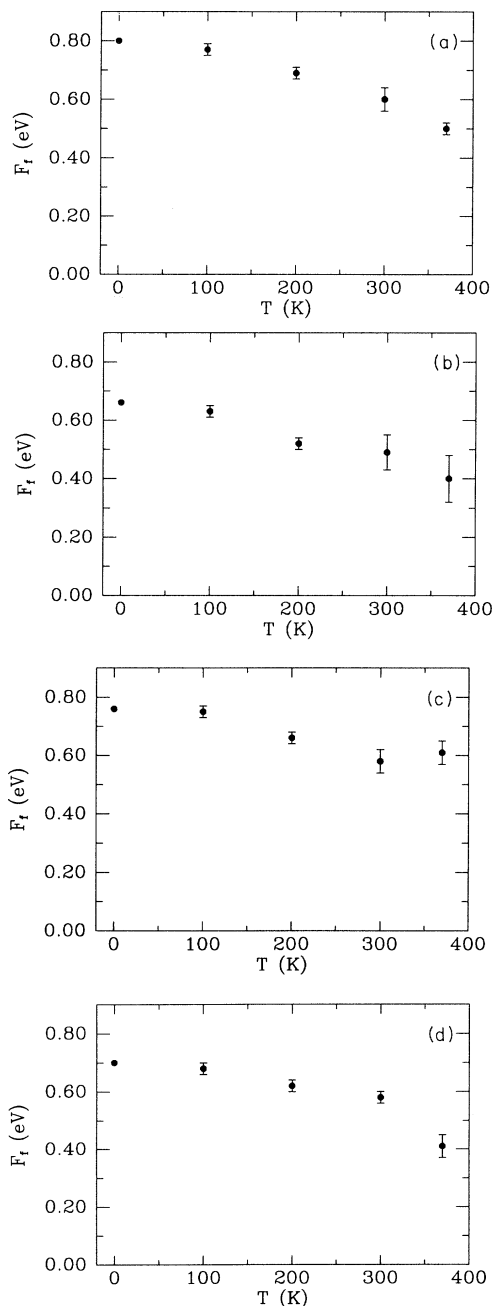


FIG. 5. As Fig. 4, for the four kinds of divacancy: (a) D_1 , (b) D_2 , (c) D_3 , (d) D_4 .

3. Interstitial

Figure 6 shows the formation free energy of the (111) dumbbell with $S^{\text{or}} = k_B \ln 10$. Arguments have been presented in the past (see, e.g., Ref. 6 and references therein) in favor of a negative formation entropy for the interstitial, as its presence compresses the lattice and might be expected to lead to higher phonon frequencies and thus lower entropy. Our data do not support this view. Indeed, the formation free energy drops rapidly with T , suggesting a quite large, positive formation entropy, possibly $6k_B$ or $7k_B$. At $T = 370$ K, F_{fI} is close to zero; although this is not conclusive, due to the large statistical fluctuations at that temperature, it clearly suggests that the interstitial may play a significant role close to the melting point. Indeed, one may suggest a view of melting in Na, if not an actual mechanism, as the destabilization of the crystal lattice towards the formation of interstitials.

IV. CONCLUSIONS

We have shown the results of a fully *ab initio*, self-consistent calculation of defect free energies in a metal. The method we used allows one to reach easily the large cell sizes and long simulation times required by this kind of problem: All the calculations were performed on a Convex 200 and are comfortably within reach of a powerful workstation.

Our results are in good agreement with previous calculations at $T = 0$, and represent a significant extension of them. In particular, it has been shown that the role of interstitials at equilibrium cannot be dismissed as static calculations suggested. Indeed, the increase in the number of interstitials might be at the root of the increase in the self-diffusion coefficient of sodium close to melting. To resolve such questions, a dynamical calculation of the defect-induced self-diffusion for the various mechanisms should be performed. Work is in progress along these lines.

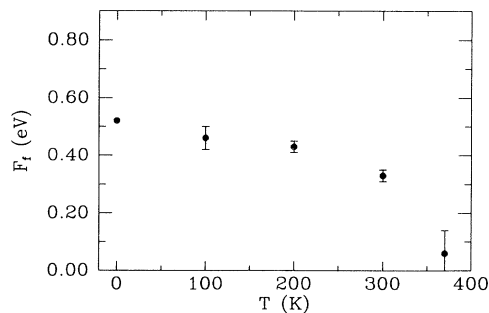


FIG. 6. As Fig. 4, for the interstitial.

Experimental evidence of simultaneous contributions from vacancies and divacancies to the self-diffusion find an interpretation as the presence of a "vacancy gas" in equilibrium with "vacancy molecules" which continuously bind and dissociate after some time. A quantitative theory, however, appears difficult to formulate, as the energy differences are tiny and one would need very accurate results.

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* Present address: Laboratoire de Physique, Ecole Normale Supérieure de Lyon, 46 Allée d' Italie, 69364 Lyon Cédex 07, France.

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