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Defect Energetics for Self-Diffusion in Sodium[*]

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Recent data on self-diffusion and the isotope effect in sodium indicate clearly the existence of at least two operating defect mechanisms. This paper investigates the possibility of vacancy, divacancy, and interstitial mechanisms by calculating the diffusion energetics for the vacancy-type defects and estimating the same for interstitials based on other calculations. The aim is to search for a combined mechanism which can be used to interpret the available data on defect studies. The validity of choosing pseudopotentials for defect calculations is tested by using three potentials with different exchange and correlation corrections in the dielectric function of the conduction electrons. There is about a 15% variation in the results for vacancy and divacancy. Our energetic results indicate that a combined vacancy and divacancy mechanism can be used to account for most of the data obtained in diffusion, isotope effect, and dilatometric measurements. The available theoretical and experimental results do not seem to favor, but cannot completely rule out, the interstitial mechanism. It is suggested that the question is not likely to be resolved by further energetic calculations due to the lack of reliable interatomic potentials at close ranges; instead, experiments designed for detecting interstitials and dynamical calculations of ΔK are needed.

I. INTRODUCTION

Currently there is considerable interest in studying diffusion and defect energetics in sodium. The primary objective of these investigations is to gain a basic understanding of the diffusion mechanisms operative in bcc metals by studying a typical simple metal, such as sodium. The experimental studies cover a variety of techniques, such as diffusion measurements,[1,2] isotope effects,[1,2] dilatometric measurement,[3] NMR,[4] cold-work annealing,[5] defect-resistivity measurement,[6] and defect-specific-heat measurement.[7] Some of these experiments have been carried out over extensive ranges of pressure and temperature. In Table I, the results of most of these experiments are summarized. The following characteristics, which are important to the study of diffusion mechanisms in

TABLE I. Summary of experimental results of defect studies in Na.

(A) Diffusion studies

(1) Temperature measurements

T(°C)	D_0 (cm^2/sec)	Q(eV)	Remarks
0 to 97	0.145	0.44	Ref. 2
	0.72	0.51	Ref. 1 (two-exponential fit)
	0.0057	0.37	
−78.5 to 97	8	0.62	(three-exponential fit)
	0.144	0.48	
	0.009	0.38	
14.8 to 117.1	0.085	0.49	Ref. 1 (at 7000 atm)

(2) Pressure measurements

T(°C)	V_a (Ω_0)	Percent of contribution	
14.8	0.70	7	
	0.76	29	Ref. 1. (pressure from 1 to 9500 atm)
	0.33	64	
91.3	0.68	28	
	0.68	36	
	0.27	41	

(3) Isotope effect

T_m(°K)/T(°K)	$f\Delta K$	
1.043	0.329	Ref. 1 (more data were presented than given here.)
1.073	0.351	
1.548	0.394	

(B) Other measurements on vacancy properties

Formation energy (eV)	Formation volume (Ω_0)	Migration energy (eV)
0.42 (Ref. 3)	0.41 (Ref. 4)	0.03 (Ref. 5)
0.40 (Ref. 6)		
0.36 (Ref. 7)		

sodium, are observed.

(1) The Arrhenius diffusion plot for sodium exhibits very pronounced curvature at high temperatures. Analysis of the temperature and pressure data reveals that the high-temperature process has about twice the activation energy and volume for diffusion in comparison to the low-temperature process. The former contributes about 33% to diffusion at 15 °C and increases to 60% at 90 °C.

(2) The dilatometric data clearly indicate the dominant defect to be of vacancy type even though the presence of interstitials cannot be completely ruled out. The formation energy of the dominant type of defect was found to be only a few hundredths of an eV smaller than the activation energy for diffusion, so these defects should have low migration energy.

(3) The parameter $f\Delta K$, measured by isotope-effect experiments, is not constant as a function of temperature, but decreases quite sharply near the melting point. The general downward trend of $f\Delta K$ is steeper at 7000 atm than at 1 atm.

These results clearly indicate that more than one type of point defect contributes to diffusion. It is, therefore, not sufficient, in the study of diffusion mechanisms, to consider only one kind of point defect, but rather it is necessary to include two, or even three, kinds of defects. It is also important that the pressure data be taken into account in addition to the temperature data. The proposed mechanism(s) must be capable of accounting for the defect behavior under varying temperature as well as pressure.

Most of the previous calculations defect energetics were published before Mundy reported his recent results,[1] so the emphasis has been focused on one of two types of defects, either vacancy or interstitial. Except for the classical work by Fumi[8] on the vacancy formation energy and some early calculations on the vacancy configuration,[9] most of the recent calculations use effective interionic potentials constructed according to pseudopotential theory. These include calculations of diffusion energetics for the vacancy and interstitial,[10,11] the vacancy formation energy and volume,[12] the migration configuration energy,[13] and, most recently, the diffusion energetics for the divacancy.[14] Calculation of ΔK has been carried out by Achar,[15] Brown *et al.*,[11] and Huntington *et al.*[16] for the vacancy, all using the reaction-rate theory formulated by Vineyard.

There has been considerable argument on the question of whether an interstitial or vacancy should be the most likely mechanism for diffusion. Brown *et al.*[11] argued that the vacancy is not likely since their calculated migration energy (about 0.2 eV) and ΔK (very close to unity) are too high compared to the experimental values, about 0.03 eV and 0.5, respectively. They proposed the interstitial mechanism of the ⟨111⟩ crowdion via intermediate ⟨1$\bar{1}$0⟩ split configurations. The reasoning of this proposal is questionable. First, there are other calculations, based on different interatomic potentials, which give a vacancy formation energy of 0.35 eV (Ref. 12) and a migration energy of 0.07 eV,[10] the sum of which is close to the measured activation energy. Secondly, Feit[17] recently showed that the large ΔK is a characteristic feature of the reaction-rate theory, but not for the dynamical theory of diffusion. Huntington *et al.*[16] have applied the reaction-rate theory quite extensively to calculate ΔK for bcc crystals. They found that regardless of whether a Born–Mayer potential or a pseudopotential is used, the value of ΔK is always very close to unity, about 0.95. The result is independent of the exact relaxation around the saddle point. Based on the dynamical theory of diffusion, Feit[18] subsequently estimated ΔK for the vacancy in sodium and obtained a low value of 0.5. It is clear that a vacancy mechanism cannot be ruled out especially when the dilatometric measurement indicates dominant vacancy-type defects. Feit[17] suggested a combined vacancy and divacancy mechanism but with interstitials operating at low temperatures.

In light of Mundy's recent data, it appears to be very useful to carry out calculations as complete as possible for the diffusion energetics of different defects in sodium. The goal is to find a diffusion mechanism which is consistent with the available temperature and pressure data. This is one of the objectives of this paper. The defects studied are the vacancy, divacancy, and interstitial. Another objective is to assess the reliability of such theoretical calculations based on different interatomic potentials. Such evaluation of theory is probably overdue for sodium, particularly in view of the recent advance in the theory on the dielectric function for simple metals.[19,20] For this purpose, we have used potentials constructed by the same bare-ion pseudopotential but screened by three different dielectric functions.

II. CALCULATION OF DEFECT ENERGETICS

The method of calculating defect energetics is formulated within the framework of the pseudopotential theory. Except for the migration of a vacancy, the procedures for calculating the energetics for vacancy formation[12] and divacancy diffusion[14] have been described previously, so the methods will not be described in detail here.

In the pseudopotential theory, the total lattice potential can be separated into volume-dependent and structure-dependent energies. The latter can be expressed as a sum of the two-body interionic potentials. Its magnitude depends on the detailed atomic arrangement of the lattice. The two-body potential, being called the effective interionic potential, consists of the direct Coulombic potential plus the indirect ion-ion interaction due to the screening by the conduction electrons. This effective potential is of the central-force type for a local pseudopotential. However, due to the presence of the volume-dependent energy, the Cauchy relation does not have to be satisfied, nor does the equilibrium of the lattice have to be maintained solely by the interionic potentials.

The general procedure for defect calculation consists of three steps. First, the defect configuration is set up by removing an interior atom at lattice site to the surface for formation calculation. For forming a divancy, two interior atoms have to be removed. The energy required for rearranging atoms is called the configuration energy; it is the change in the structural energy due to a different configuration. The second step is to calculate the relaxed configuration around the defect. A modified lattice-statics method[21] is used; it is formulated within the framework of pseudopotential theory.[12] This method obtains a minimum energy configuration by relaxing all atoms simultaneously, but the displacements and the relaxation energy are calculated only to the harmonic order. Finally the whole defect-lattice complex is relaxed uniformly to an equilibrium configuration. In the last step, the defect volume can be calculated. The sum of the energy contributions from each of these steps gives the defect energy. In the first and the final steps, there are contributions from the volume-dependent energy due to changes in electronic density and atomic volume. This energy is important in determining the defect volume and should be carefully treated.

To illustrate the procedures, the calculation of the migration energy is briefly described. The configuration during migration can be expressed via the following structure factor:

$$S'(q)=\frac{1}{N}\left(\sum_{l}^{N+1} e^{-i\vec{q}\cdot\vec{r}^{l}}-e^{-i\vec{q}\cdot\vec{r}^{v}}-1+e^{-i\vec{q}\cdot\vec{r}^{a}}\right),$$

where $\vec{r}^{a}$ designates the position of the moving atom which migrates from the origin to the vacant site $\vec{r}^{v}$, and $\vec{r}^{l}$ is the lattice vector. Substituting $S'(q)$ into the structure-dependent energy and calculating the energy difference from the lattice containing one vacancy, one obtains the configuration energy for vacancy migration, E_c^v. Since the structure energy is usually written as a lattice sum in the reciprocal lattice space, E_c^v can be expressed as a sum and an integral in the q space, a procedure used in a previous calculation [see Eqs. (3.4) and (3.5) in Ref. 13]. However, if one carries out the integration, the following simplified expression can be derived after some manipulation:

$$E_c^v=\sum_{l}{}'\left[V(|\vec{r}^{l}-\vec{r}^{a}|)-V(|\vec{r}^{l}-\vec{r}^{v}|)\right],$$

where $V(r)$ is the effective interionic potential and the prime over the summation indicates that the terms when $l=0$ and v are excluded. By calculating E_c^v for $\vec{r}^{a}$ from the origin to $\vec{r}^{v}$, one can map out the unrelaxed potential barrier for vacancy migration. The migration energy calculation is completed by using the lattice-statics method to calculate the relaxation energy and displacements at the saddle point. The relaxation at the saddle point cannot be neglected, as done in Ref. 13, since, when included, it reduces significantly the migration energy. The relaxation contribution is the difference in the relaxation energies of the saddle point and an isolated vacancy. For Na, it is about half of E_c^v. The displacements of the atoms on the two bottleneck triangles turn out to be as high as 7% of the radial distance. With such a large relaxation, the anharmonic correction to both the displacement and energy should be more important than for vacancy formation. The correction due to the third-order terms usually reduces the numerical results obtained in the harmonic approximation. The correction can be crudely estimated based on the ratio of the measured second- and third-order elastic constants. We found the correction to be about 15%. However, it is expected that if the fourth-order terms are included, this 15% correction would be reduced. In the present investigation, none of these anharmonic corrections was included.

Once the relaxed configuration of the saddle point is determined, the migration volume can be calculated by minimizing the total lattice energy of the saddle-point lattice with respect to a uniform dilatation. The volume-dependent energy is important in determining the amount of dilatation, and so the migration volume, but it does not contribute to the migration energy to the first order of lattice dilatation since the starting configuration for migration, the relaxed vacancy, is already at equilibrium.

The calculation of the diffusion energetics for divacancy is complicated by the existence of several stable divacancy configurations in sodium and the peculiar jumping geometry in a bcc lattice. These stable configurations differ in binding energy only of the order of kT, the thermal energy at diffusion temperatures. The jumping geometry in bcc lattice is such that a nearest-neighbor jump always dissociates a first-neighbor divacancy to other configurations. As a result, the calculation has to be extended beyond the nearest-neighbor divacancy, and energetically favorable paths have to be sought among jumps connecting various configurations. For details, see Ref. 14. In the present study, calculation for each potential has been extended to include the first five-neighbor divacancies.

The principles of calculation of diffusion energetics for interstitials are quite similar to those of vacancies. For sodium, Torrens and Gerl[10] have calculated the migration energy for an interstitial by using the potential with the Hubbard–Sham dielectric screening, being called the HS potential here. They found a minimum migration energy of 0.005 eV for the octahedral interstitial. Based on a different potential, Brown *et al.*[11] found the ⟨111⟩ crowdion to be most stable, and its migration requires an energy of 0.0005 eV. It is significant in these results that the migration energies are very small, so interstitials are highly mobile at the diffusion temperatures. The factor deciding which interstitial actually migrates then depends on the relative magnitude of the formation energy. It is at this point that the reliability of the calculation becomes questionable. The difficulty is mainly due to the unreliable nature of the close-range interatomic potentials. There the potential is very large compared to that at the atomic positions and not well known, but it is extremely important in determining the formation energy. Unfortunately, the difficulty is quite intrinsic since the potential in the close range is not accessible by measuring the properties of a perfect lattice. In view of such a difficulty, we have not carried out detailed energetic calculations for interstitials. Our attempt to assess the importance of the interstitial contribution to diffusion is based on the results of Torrens and Gerl[10] and Brown *et al.*[11]

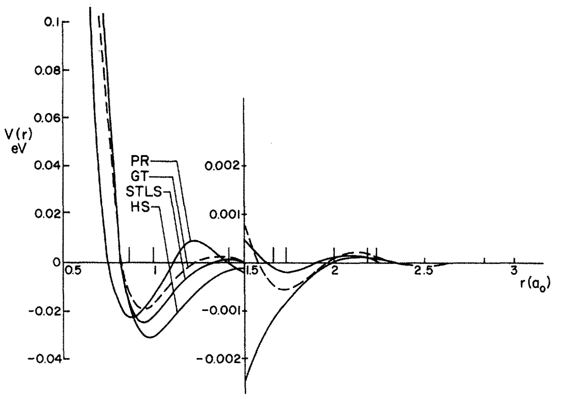


FIG. 1. Comparison of interatomic potentials used for defect energetic calculations in sodium. The potentials used in the present study are designated the HS, STLS, and GT potentials and are constructed according to different dielectric functions. The PR potential was used by Brown *et al.* in their calculation.

III. SELECTION OF THE POTENTIAL

In our previous defect calculations,[12,14] we have used a pseudopotential with model parameters determined by fitting to the elastic constants.[22] The bare-ion potential is of the local Heine–Abarenkov type and the dielectric function is corrected approximately for electron exchange and correlation effects according to the Hubbard–Sham scheme.[23] This effective interionic potential was also adopted by Torrens and Gerl in their calculation.[10] It will be used again in this study as a basis for comparing the energetic results calculated from two other potentials.

Recently, considerable progress has been made in applying self-consistent schemes to calculating the correlation and exchange effects in the dielectric function. Several authors[24] investigated the effects of these many-body corrections in predicting the properties of the perfect crystal. They found the effects to be important and indicated that these corrections must be properly taken into account to ensure good results. We have, therefore, also chosen in our calculation the two recent dielectric functions developed by Singwi *et al.*[19] (STLS) and Geldart and Taylor (GT).[20] These two versions have improved the HS treatment by using different self-consistent schemes to include the Coulomb correlation effects. For convenience of comparison, we shall not change the bare-ion po-

TABLE II. Comparison of the results of vacancy diffusion energetics.

(A) Formation energetics

Dielectric function used	Relaxation energy E_r^v (eV)	Formation energy E_f^v (eV)	Formation volume V_f^v (Ω_0)
HS	-0.05	0.35	0.60
STLS	-0.04	0.30	0.65
GT	-0.03	0.27	0.71

(B) Migration energetics

Dielectric function used	Configuration energy E_c^v (eV)	Saddle-point relaxation energy E_r^m (eV)	Migration energy[a] E_m^v (eV)
HS	0.12	-0.12	0.05
STLS	0.14	-0.09	0.09
GT	0.14	-0.07	0.10

[a] Migration energy $E_m^v = E_c^v + E_r^m - E_r^v$.

tential throughout the calculation.

In Fig. 1 we compare the effective interionic potentials used in our calculations. These potentials are very similar in the over-all form compared to that based on Ashcroft's empty core pseudopotential.[25] All three potentials reproduce very well the phonon dispersion curves, elastic constants, and cohesive energy for the perfect lattice. The shape of the potential minimum is quite different for different dielectric functions. This implies that the relaxation energies for vacancy-type defects can vary considerably when calculated according to these potentials. However, since these potential wells are quite shallow, about 0.02 to 0.03 eV, the variation in defect energetics cannot be too large. All these potentials have similar long-range oscillations beyond the fifth-neighbor position and the magnitude of these oscillations is less than 0.001 eV. This shows that the long-range defect displacement fields should be quite similar but insignificant in contributing to defect energetics. The above observations based on the general form of the potential have indeed been borne out in the results for vacancy-type defects. The situation is different for interstitial energetics. At half the lattice parameter, the HS potential exceeds the GT potential by 0.1 eV, which is about the difference in the interaction energy between the interstitial and a nearest atom. Therefore, depending on the number of nearest atoms, the interstitial energetics if calculated would have been very different.

For completeness, we have included in Fig. 1 the LRO-2 potential used by Brown *et al.* in their calculation.[11] This potential was determined earlier by Paskin and Rahman[26] (PR) based on a radial density function in liquid sodium measured by neutron diffraction techniques. Compared to the pseudopotentials, this potential has a softer core repulsion, much larger long-range oscillations, and closer interatomic distance for the first minimum. All these factors turn out to have substantial effects on the results of defect energetics, as is evident from the difference between their results and ours. The PR potential was determined by fitting a Born-Mayer potential originally used by Fuchs[27] in an elastic-constant calculation to an asymptotic expression of the Friedel oscillation. The magnitude and phase of the oscillating potential were used as adjustable parameters.

IV. RESULTS

Using the potentials in Fig. 1, we have calculated the energy, volume, and displacement field for the formation and migration of the vacancy and divacancy. Here we report the results of the defect energy and volume. Detailed comparison of the displacement field and energetics and their dependence on the potential will be deferred to a forthcoming paper.

The results of the energetics of vacancy diffusion are compiled in Table II. Among the three potentials, the HS potential gives highest formation and relaxation energies and lowest configuration energy for migration, as compared to the STLS potential and GT potential in the order of magnitude. The formation energy varies from 0.35 to 0.27 eV and the activation energy from 0.41 to 0.37 eV for the vacancy; the range of the variation is about 20% for the formation energy and 10% for the activation energy. In all cases, the vacancy was found to migrate by jumping directly to the nearest-neighbor position with the saddle point at the middle of the jump. We have calculated the migration volume according to the HS potential and obtained a value of $0.08\ \Omega_0$.

The results of the divacancy energetics are summarized in Tables III and IV. Only the formation energies for the stable divacancies are given in Table III. The second-nearest-neighbor (2NN) divacancy turns out to be the most stable configuration with a formation energy that varies from 0.67 eV for the HS potential to 0.52 eV for the GT potential. The migration of this divacancy is found to be via a direct nearest-neighbor (NN) jump into a NN divacancy. To continue the migration process, the NN will return to a 2NN configuration via a nearest-neighbor jump. Another cyclic jump of 2NN → 4NN → 2NN is also found to be energetically favorable, with a migration energy only about 0.02 eV higher than that between NN and 2NN divacancies. In either one of these jumping cycles, the forward and the reverse jumps were found to have identical saddle-point configuration, so they have the same activation energy and volume, hence not separable by diffusion measurements. In Table IV results of the divacancy migration energetics are

TABLE III. Comparison of results of divacancy formation energetics.

Vacancy[a] position	Binding energy E_b (eV)	Relaxation energy E_r^{2v} (eV)	Formation energy E_f^{2v} (eV)	Formation volume V_f^{2v} (Ω_0)
		(A) HS potential		
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	0.006	−0.093	0.70	1.3
100	0.04	−0.11	0.67	1.2
$\frac{3}{2}\frac{1}{2}\frac{1}{2}$	0.007	−0.11	0.70	1.2
		(B) STLS potential		
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	0.006	−0.07	0.60	1.3
100	0.03	−0.085	0.58	1.3
$\frac{3}{2}\frac{1}{2}\frac{1}{2}$	0.006	−0.084	0.60	1.3
		(C) GT potential		
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	0.006	−0.055	0.53	1.4
100	0.017	−0.064	0.52	1.4
$\frac{3}{2}\frac{1}{2}\frac{1}{2}$	0.006	−0.066	0.53	1.4

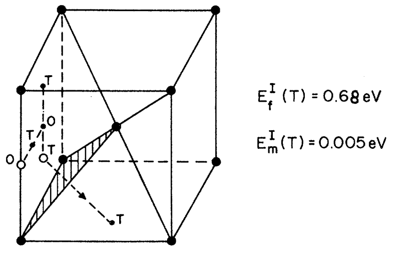
[a] This is the position of one of the vacancies; the other is at the origin.

TABLE IV. Comparison of results of divacancy migration energetics.

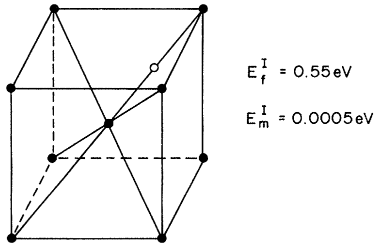
	1NN→2NN	2NN→1NN	4NN→2NN	2NN→4NN
		(A) HS potential		
E_c^{2v} (eV)	0.09	0.11	0.11	0.13
E_m^{2v} (eV)	0.04	0.07	0.06	0.09
		(B) STLS potential		
E_c^{2v} (eV)	0.11	0.12	0.12	0.13
E_m^{2v} (eV)	0.08	0.10	0.09	0.11
		(C) GT potential		
E_c^{2v} (eV)	0.12	0.13	0.13	0.14
E_m^{2v} (eV)	0.09	0.11	0.10	0.11

given for the three potentials studied. It is interesting to note that the migration energy for the divacancy is path dependent and not necessarily smaller than that of a vacancy. The diffusion activation energies for these divacancies can be obtained by summing the formation and migration energies.

The results on the interstitial energetics are shown in Fig. 2. The formation energy for the tetrahedral interstitial is obtained by combining Torrens and Gerl's[10] value of formation energy for a Frenkel pair, 1.03 eV, and our E_f^v calculated according to the HS potential, 0.35 eV. According to these authors, among the three possible migration paths shown, the energetically favorable path is the migration of the tetrahedral interstitial through the shaded atomic triangle, and the energy required is 0.005 eV. The results of the ⟨111⟩ crowdion were obtained by Brown *et al.*, [11] who found this interstitial to be more stable than the ⟨110⟩ as well as the ⟨111⟩ split interstitials. However, the formation energies for these interstitials are found to be very close, with difference less than 0.01 eV. Their results indicate that at the diffusion temperatures, there is probably no dominant type of interstitial, and several configurations of interstitials can contribute to diffusion. In fact, it was proposed that the diffusion of the crowdion will occur frequently via an intermediate ⟨110⟩ split interstitial configuration. The migration energy for the ⟨111⟩ crowdion was found to be only 0.0005 eV, even smaller than that of the tetrahedral interstitial. All the interstitial results quoted here were calculated by using the LRO-2 potential rather than the LRO-1 potential. According to Paskin and Rahman, [26] the former gives better fit to the radial distribution function and diffusion coefficient in liquid sodium.



Tetrahedral and Octahedral Interstitials



⟨111⟩ Activated Crowdion

FIG. 2. Results of diffusion energetics for interstitials in sodium. The results of the tetrahedral and octahedral interstitials were obtained by Torrens and Gerl based on the HS potential. The results for the ⟨111⟩ activated crowdion were obtained by Brown *et al.* according to the PR potential.

V. DISCUSSION

Based on the present results of defect energetics, it appears that the data of self-diffusion and other defect studies in sodium can be most consistently interpreted in terms of a combined vacancy and divacancy mechanism. The best supporting evidence lies in the agreement between the measured and the calculated energies for diffusion. The calculated activation energies for diffusion range from 0.37 to 0.40 eV for the vacancy and from 0.62 to 0.74 eV for the divacancy. These values are in good agreement with Mundy's temperature data.

For the activation volume, if the migration volumes of these defects were taken to be both less than $0.1\Omega_0$, the diffusion volume of the divacancy is found to be about twice that of the vacancy. This is consistent with the pressure measurement on diffusion. The theoretical value of the formation volume exceeds the measured values by about 75%. The discrepancy is not understood at present.

Another piece of supporting evidence is the agreement between the dilatometric data and the calculated defect formation energies. Feder and Charbnau[3] have analyzed their dilatometric data according to the presence of both the vacancies and the divacancies. They found that an excellent fit to the data can be obtained by taking a vacancy formation energy of 0.40 eV and a divacancy binding energy of 0.04 eV, and formation entropies of $5.5k_B$ and $11.0k_B$, respectively. Our theoretical results are in good agreement with the measured energies. Even though the choice of the defect energies in such analysis is by no means unique, the fitting exercise has nevertheless shown that the dilatometric data can be consistent with vacancy- and divacancy-type defects.

We have analyzed the temperature variation of $f\Delta K$ based on vacancy and divacancy diffusion mechanisms. For the correlation factors, we took 0.727 for the vacancy, and used a formula obtained by Mehrer *et al.*[28] to calculate the temperature variation of f for divacancy jumps between NN and 2NN configurations. Using a least-squares analysis, we found that except for the highest-temperature point, the temperature variation of $f\Delta K$ can be fitted well within the experimental error by taking ΔK to be 0.59 for vacancy and 0.58 for divacancy. Both these ΔK values appear to be reasonable for vacancy-type defects judging from Feit's estimate based on the dynamical theory of diffusion.[17]

One reason put forth by Brown *et al.* for supporting interstitial mechanism is in the magnitude of the migration energy. Their calculated vacancy migration energy, 0.19 eV based on the LRO-2 potential, is several times higher than the measured value, estimated to be 0.03 eV according to Guggan[5] or from the difference between the diffusion activation energy and the formation energy. Since the calculated migration energy for the interstitial is very low, it was suggested that the formation energy of the interstitial should be equal to the measured diffusion activation energy and the interstitial is the operating mechanism in diffusion. This proposal is difficult to justify for two reasons. First, the migration energy calculated does not have to be as high as that of Brown *et al.* Based on different interatomic potentials, our migration energy varies from 0.05 to 0.10 eV, depending on the dielectric function used. These values are considerably higher than the measured migration energy, but the discrepancy is within the experimental error limits. In any case, the agreement is not worse than the migration energy obtained by Brown *et al.* for interstitials. Secondly, it was emphasized that the dilatometric data can be interpreted in terms of a vacancy and interstitial model, but according to the energies and entropies assumed by Brown *et al.*, the interstitial concentration would be less than 1% of the vacancy. Based on these conditions, we estimate that compared to vacancies, the interstitials cannot dominate diffusion at room temperature, even with a vacancy migration energy as high as 0.10 eV.

There are difficulties in using only vacancy and divacancy mechanisms to interpret all of the diffusion data, particularly in explaining the pressure data of the isotope effect. Using similar procedures as in the analysis of the temperature data of the isotope effect, the values of ΔK obtained by analyzing data at 7000 atm were not consistent with the values at 1 atm. In fact, a ΔK of -0.6 was obtained for the divacancy (0.59 for vacancy) in a least-squares analysis of the data compiled in Table VI of Mundy's paper. A negative ΔK value appears to be unphysical. The problem probably lies in the vacancy-divacancy model or in the difficulty of obtaining accurate isotope-effect data under pressure. At present, we have no satisfactory explanation for the discrepancy.

The other difficulty is in explaining the origin of a possible third mechanism at an intermediate temperature range as indicated in Mundy's data analysis. As mentioned, Feit[17] suggested that it is due to a single vacancy. The major difficulty with this proposal is that the activation volume measured for the intermediate temperature range is almost exactly the same as the high-temperature divacancy mechanism. This evidence casts serious doubt on the validity of the assigned vacancy mechanism. In addition, the energetic results for vacancy diffusion as obtained in the present investigation are in better agreement with the low-temperature process than that at intermediate temperatures. The alternative would be to assign the intermediate-temperature process to the interstitial. The advantage would be the association of the interstitial with an activation volume about twice that of the vacancy and also with a higher activation energy, which presumably can be due to the higher formation energy for interstitials. There would not be much difficulty in explaining the low values of $f\Delta K$ since ΔK for interstitials is thought to be close to $\frac{1}{2}$.[11]

Before investigating this proposed mechanism, one must first question the reliability of using least-squares analysis to predict the existence of three independent diffusion processes. Mundy[1] mentioned that his three-exponential fit to the temperature data was not as satisfactory as the two-exponential fit. The six parameters in the fit can be varied over a wide range without change in the goodness of the fit. It appears that the existence of the intermediate mechanism is questionable. In any case, any attempt to establish an interstitial mechanism by energetic calculations is seriously hindered by the difficulty of obtaining reliable close-range interatomic potentials.

Considering the interstitial formation energies quoted here, the value obtained by Brown *et al.* is about 20% less than that obtained by Torrens and Gerl. This discrepancy can be understood because the PR potential at short ranges is considerably softer than the HS potential (Fig. 1). However, reliability of the short-range portion of the PR potential is more uncertain. It is the same Born–Mayer potential determined by Fuchs in an early calculation of elastic constants.[27] It can be seen from Fuchs's results that the contributions from the Born–Mayer potential to elastic constants are very small, so the close-range potential cannot be accurately determined under these circumstances. It appears reasonable to believe that the formation energy of interstitial is closer to 0.68 eV than to 0.55 eV. This makes it difficult to assign the intermediate-temperature mechanism to interstitials.

In conclusion, we feel that by comparing the measured and the calculated defect energetics, the vacancy-divacancy model is the most satisfactory mechanism for diffusion in sodium. Circumstances do not completely rule out the interstitial mechanism. However, further efforts in calculating interstitial energetics do not seem to be fruitful, because of the limitation on the knowledge of the short-range interatomic potentials. Instead, experiments specifically designed to measure interstitial contribution in diffusion, such as the NMR experiment originally suggested by Mundy,[1] or possibly internal friction measurements, are needed to resolve the interstitial question. More work is also required in applying the dynamical theory of diffusion to calculate ΔK factor for vacancy as well as interstitial type defects in sodium.

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