The calculation of vacancy formation energies in the alkali metals Li, Na and K

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Abstract. The formation energies of vacancies in Li, Na and K have been calculated as functions of temperature using pair potentials determined from first principles. Included in the calculation is a term describing the change in entropy upon formation of the defect. This term is of critical importance in obtaining the right temperature dependence. When combined with earlier calculations of migration energies, the results agree very precisely with the measured self-diffusion energies, giving strong support to the single-defect mechanism for diffusion. On the other hand the calculated formation energies do not agree particularly well with the published measurements, leading to the suggestion that a re-interpretation of these experimental results would be useful.

1. Introduction

Conceptually, vacancy formation is one of the simplest defect processes to visualise in a crystal; an atom is simply removed from some position within the bulk of the crystal and transferred to the surface and the system relaxes under the influence of the interionic forces. The formation energy is then the difference between the energies of the perfect and defect crystals. Unfortunately, in metals, even the zero temperature or static calculation of this quantity turns out to be surprisingly complex. This is because of the participation of the conduction electrons in the formation process. Recognising this fact, the earliest calculations pioneered by Huntington and Seitz (1942) (also Huntington 1942) focused on the change in electronic wavefunctions near a vacancy. More recently, using the same philosophy, Fumi (1955) adopted a jellium approach, later extensions of which have led ultimately to proper self-consistent treatments of the jellium model such as those of Manninen *et al* (1975) and Robinson and de Chatel (1975). We refer the reader to the review by Evans (1976) for a detailed analysis of this approach which, although it contains some of the essential features of vacancy formation in metals, does not seem capable of yielding quantitative results.

A second approach to the vacancy formation energy was suggested by Harrison (1966) using pseudopotential theory. Treating the pseudopotential as a perturbation and writing the total energy of the nonvibrating lattice E_0 to second order in the perturbation, one obtains E_0 in the form

$$E_0 = E_1(\Omega) + \frac{1}{2} \sum_{l \neq l'} V(|r_l - r_{l'}| \Omega) \tag{1.1}$$

where $E_1(\Omega)$ is a function only of the volume Ω of the system and $V(|r_l - r_{l'}|, \Omega)$ is an effective pair potential describing the interaction between two ions at positions r_l and $r_{l'}$. These positions need not be lattice sites. An important point is the fact that the pair potential is a function of the volume. This comes about because the conduction electron screening of the bare ion–ion interaction which gives rise to $V(r, \Omega)$ is a function of the electron density. Now one can in principle determine the vacancy formation energy ΔE using equation (1.1) simply by evaluating it for the perfect crystal and for the defect crystal and taking the difference between these two results. Unfortunately this procedure is not completely straightforward for a number of reasons. One is that the pair potentials are very long-ranged and truncation of them at short distance can lead to serious errors. A second is that, upon formation of the vacancy, the volume of the system changes and one must include in the calculation the change in $E_1(\Omega)$ which is usually not known with sufficient precision for quantitative calculations. Finally a third and potentially more serious problem arises when one realises that the removal of an ion plus associated charge cloud from a lattice site, in general, leaves a vacancy with a local depletion of charge. Keeping in mind that $V(r, \Omega)$ is really a function of the density of the electrons that are screening the ions, this implies that, in the immediate neighbourhood of the vacancy, $V(r, \Omega)$ is altered in some manner which is not all clear. This problem is particularly serious in polyvalent metals but in fact may not be significant in monovalent metals. This is because the changes in electron density in the neighbourhood of a vacancy will be much less for a monovalent metal than for a polyvalent metal, resulting in much smaller values of $\nabla n(r)$, where $n(r)$ is the density. If these gradients of $n(r)$ can be described by linear response theory, then they are automatically taken into account by the dielectric function that screens the bare-ion pseudopotential (Geldart *et al* 1972). Consistent with the conclusions of Evans and Finnis (1976) we shall assume this to be the case in the alkali metals and ignore the possibility that the pair potential should be altered in the vicinity of the vacancy.

The long-range parts of the pair potentials can be handled by suitably damping them (Duesbery, Jacucci and Taylor 1979) (DJT) and this particular aspect of simple metal potentials does not pose any serious difficulty once it is recognised.

To deal with the problems associated with $E_1(\Omega)$ one can take advantage of the idea introduced by Chang and Falicov (1971) to evaluate the vacancy properties at constant volume. The desired constant pressure defect formation (or migration) parameters are then deduced with the help of the thermodynamic equilibrium condition on the free energy. It is easily shown (see Appendix A) that the formation Gibbs free energy at constant pressure ΔG_p is equal to the Helmoltz free energy difference at constant volume ΔF_v. In zero temperature calculations this relation reduces to the equation of the formation enthalpy at constant pressure ΔH_p and the formation energy at constant volume ΔE_v. The great advantage of the constant volume calculation over a constant pressure calculation is that $E_1(\Omega)$ substracts out of the problem. In fact it is not difficult to show that the static component of the formation energy is given by

$$\Delta E_v = -\frac{1}{2} \sum_l{}' V(r_l, \Omega) - \frac{1}{6} \sum_l{}' r_l \frac{\partial V(r_l, \Omega)}{\partial r} \tag{1.2}$$

a formula which does not contain $E_1(\Omega)$. The first term is the usual sum over the pair potential and the second, or virial, term arises from the squeezing of the lattice in order to maintain constant Ω.

Although the idea of performing constant-volume calculations has been available for many years, the way in which it has been implemented so far, i.e. $\Delta H_p = \Delta E_v$, neglects the anharmonic properties of the lattice vibrations and limits its validity to strictly harmonic lattices, for which the vibration frequencies are independent of the volume. If the thermal expansion of the lattice is considered, as is done in quasi-harmonic calculations, then it is not valid for finite temperature because this procedure neglects the fact that the entropy is also a function of the lattice spacing. However, the validity of the method is easily extended to finite temperature by correctly applying the equilibrium condition to the Gibbs free energy of the vibrating lattice. As is explicitly shown in Appendix A, one obtains for the formation enthalpy at constant pressure ΔH_p the following relationship to the formation energy at constant volume ΔE_v:

$$\Delta H_p = \Delta E_v + T(\Delta S_p - \Delta S_v) \tag{1.3}$$

where ΔS_p and ΔS_v are the defect formation entropies at constant pressure and volume respectively. ΔH_p is the interesting quantity because it corresponds to the slope of the Arrhenius plot of the density of defects. At atmospheric pressure ΔH_p reduces essentially to ΔE_p (the formation energy at constant pressure), since the difference $p\Delta\Omega$ is negligible.

On very general grounds one expects the defect formation energy to increase with increasing temperature (Seeger and Mehrer 1969). However, quasiharmonic calculations of this quantity as a function of temperature (e.g. see Popovic *et al* 1974) invariably display the opposite behaviour. This is because of the omission of the entropy term in equation (1.3), which as we shall see later in this article plays a very important role. The relevance of this entropy term was clearly demonstrated fifteen years ago by Nardelli and Terzi (1964) in a milestone paper on the vacancy formation entropy in rare gas solids, a paper that has unfortunately not received enough attention from later authors.

In this paper we present some results of calculations of fully relaxed vacancy formation energies in the alkali metals Li, Na and K at both low and high temperatures using the pair potential formalism. It is certainly true that this problem has been studied by many authors previously to us, who frequently obtained apparently good agreement with experiment. Nevertheless we feel that our calculation is superior to those preceding because of the care taken to ensure that all effects of the long-range character of the potentials are included and because of the inclusion of the effect of the entropy of formation. In addition to these considerations this calculation is of a first-principles nature in that the pair potentials have been derived from entirely theoretical considerations with no parameters, pseudopotential or otherwise, adjusted to fit any experimental property. These are the pair potentials of Rasolt and Taylor (1975) and Dagens, Rasolt and Taylor (1975) (collectively referred to as DRT). The DRT pseudopotentials screened by the Geldart and Taylor (1970) dielectric function have been used to study a wide range of physical properties ranging from electronic transport (Shukla and Taylor 1976, Leavens 1977) on the one hand through lattice dynamics (DRT, Cohen and Klein 1975, Cohen *et al* 1976a, b) to properties of defects on the other (e.g. Schober *et al* 1975, Da Fano and Jacucci 1977, Pond and Vitek 1977), all with considerable success. It is therefore of some interest to see how well these potentials perform in a careful vacancy calculation.

In §2 we discuss some of the theoretical and computational aspects of the problem.

Then in §3 we present our results, and compare them with experiment and another calculation in §§4 and 5. Finally our conclusions are summarised in §6.

2. Theoretical and computational aspects of the problem

The starting point for a defect calculation is the interionic potential. As commented in the Introduction we have used for our calculation the DRT pair potentials. Briefly, the DRT pseudopotentials were constructed by requiring that, within first-order perturbation theory, they reproduce correctly the full nonlinear charge density induce by an isolated ion placed in an infinite electron gas. In terms of the ionic pair potential, obtained by screening the pseudopotential, this has the effect of folding into it all contributions from multiple scattering at a single ion site beyond what would normally be picked up by a straightforward application of perturbation theory. For full details we refer the reader to the DRT papers. Similarly to DRT, we employed the Geldart and Taylor (1970) dielectric function, which includes correlations, to screen the pseudopotentials. Where appropriate, we have recalculated the pair potentials at the lattice parameter corresponding to the desired temperature and we have also, in the case of Na, used the corrected pseudopotential listed by Cohen *et al* (1976b). We emphasise that these pseudopotentials have been derived entirely from theoretical considerations and that no parameters have been fitted to experimental quantities.

One unfortunate characteristic of pair potentials in simple metals is the fact that they exhibit the well known Friedel long-range oscillations, and the summation of the effects of these to convergence is by no means a trivial task. For an unrelaxed vacancy where all ions are taken to be at lattice sites, the Ewald sum technique is applicable and the sums evaluated by Duesbery and Taylor (1977) can be used to calculate ΔE_v. However, for the relaxed system a different technique such as that of (DJT) is necessary. There it is shown that the pair potential $V(r, \Omega)$ can be replaced by a damped effective potential $V_{eff}(r, \Omega)$ without significant loss of accuracy. As shown by DJT, serious errors can result in the truncation of $V(r, \Omega)$ even at very large distances when evaluating equation (1.2) for ΔE_v, yet these errors can be eliminated by using $V_{eff}(r, \Omega)$. For the Li and K calculations in this paper we have used equation (2.10) of DJT for $V_{eff}(r, \Omega)$ with the damping parameter $\alpha = 0.23$. For the Na calculation, because of the well known r^{-5} asymptotic behaviour of $V(r, \Omega)$ (e.g. see equation (2.2) of DJT), we have used the appropriately modified form of equation (2.10) of DJT with $\alpha = 0.35$.

To calculate the relaxation energy we have used a cubic box, originally of side $4a$, containing 127 particles (one has been removed to form the vacancy) and then squeezed to keep the volume per particle constant. $V_{eff}(r, \Omega)$ was truncated at $r = 3.92a$. First, the static unrelaxed energy of this 127 particle system was calculated. Then the system was allowed to relax using the procedure described in Appendix 2 and the energy recalculated. The difference between these two energies was taken to be the relaxation energy, it being argued that the errors introduced both by truncation of $V_{eff}(r, \Omega)$ and by failure to include the effects of neighbouring boxes subtract out of the problem. The relaxation energy, which is of course negative, was then added to the unrelaxed formation energy, summed to convergence, to give ΔE_v.

Analogous considerations hold for the calculation of ΔP_v, the change in pressure upon formation of the vacancy at constant volume. The equation for the pressure,

derived from the virial theorem, is very similar to equation (1.2), i.e.

$$PΩ_0 = k_B T - \frac{1}{6} \sum_l' r_l \frac{\partial V(r_l, Ω)}{\partial r} - \frac{Ω\partial}{\partial Ω}\left(\frac{1}{2} \sum_l' V(r_l, Ω)\right) + P^e(Ω)Ω_0 \quad (2.1)$$

where $Ω_0$ is one atomic volume. $P^e(Ω)$ is the volume-dependent pressure arising from the electron gas and cancels out exactly when evaluating $ΔP_v$.

Some considerations are in order at this point on static calculations and the quasiharmonic approximation. In general, the energy and virial sums in equations (1.2) and (2.1) should of course have appeared in brackets denoting statistical thermal averages. The static evaluation replaces these averages by the value of the sums corresponding to the configuration of minimum internal energy (and adds $3Nk_BT$ to the energy sums). This procedure is justified in the limit of harmonic lattice vibrations† (for a given value of the lattice parameter), but is certainly unsatisfactory above the Debye temperature $θ_D$ of the solid. For instance the value of P is observed to be strongly T-dependent at high temperatures in dynamical studies where thermal averages of the virial sum are evaluated along an isocore. Fortunately there is a large cancellation of anharmonic effects when taking differences of perfect and defect solids. The true anharmonic effects that remain are the ones really connected with the defect, and no doubt their neglect causes a certain error in $ΔE_v$ and $ΔP_v$ at high temperatures. Unfortunately their relative importance cannot be evaluated within the quasiharmonic approximation, and the validity of the static treatment above $θ_D$ still rests on the accord of its predictions with the actual thermal averages. This is a delicate point of static calculations in general, and deserves further attention.

Another way of looking at it is to point out that, by replacing the thermal average of the sums with their values for the static configuration, one neglects the vibrational contribution in equation (2.1). Now of course this can be approximated by a term containing the Grüneisen constant, but there is little point in doing this because we do not know how this quantity changes when a defect is created.

Finally we note (Appendix 1) that the calculation of the entropy term in $ΔH_p$ and the formation volume requires knowledge of the lattice expansivity $α_p$ and the isothermal compressibility K_T. These obviously cannot be computed without taking explicitly into account the electronic energy and pressure, because their values depend precisely upon the equilibrium between these terms and the corresponding ionic structure terms. We choose to take the values of $α_p$ and K_T from experiment. Of course $α_p$ is implicitly introduced in the aforementioned harmonic calculation anyway through the experimental temperature-dependent equilibrium lattice spacing. The explicit introduction of $α_p$ in computing $ΔH_p$ simply ensures that the volume dependence of the formation entropy is consistent with that of the internal energy.

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† To be precise, the quasiharmonic approximation E' to the internal energy E of a system of interacting particles about a potential energy minimum consists of the (volume-dependent) potential energy E_0 of the configuration corresponding to the bottom R_0 of the potential well plus a (volume-dependent) vibrational energy E_{ll}, that can be expressed in terms of the eigenfrequencies at R_0. At temperatures larger than the Debye temperature E_{ll} tends to $3Nk_BT$ and can be dropped in performing energy differences. As a matter of fact $ΔE_{\text{ll}}$ has been found to be negligible in comparison with $ΔE_0$ in defect calculations (Gilder and Audit 1977). A clear discussion of the quasiharmonic approximation is found in an excellent book on point defects and diffusion (Flynn 1972). The significance of the entropy term of equation (1.3) is also discussed therein.

3. Results

In table 1 we present our results for the formation energies of vacancies in Li, Na and K. To calculate the unrelaxed constant volume formation energy ΔE_v^u from equation (1.2) we performed the infinite sum by using $V_{\rm eff}(r)$ summed to convergence. We would of course obtain the same answer using $V(r)$ but with enormous expenditure of effort. We also calculated ΔE_v^u in a different way using the symbol $\Delta \tilde{E}_v^u$ to denote the result. We removed one particle from the 128 contained in the box of side $4a$ and compressed the box to give the same volume per particle as for the perfect lattice. Using $V_{\rm eff}(r)$, truncated at $r = 3 \cdot 92a$, we evaluated the energy per particle ϵ^d of this new system. This then enabled us to obtain our desired result, $\Delta \tilde{E}_v^u = 127(\epsilon^d - \epsilon^0)$ where ϵ^0 is the energy per particle of the perfect lattice. The results displayed in table 1 show that ΔE_v^u and $\Delta \tilde{E}_v^u$ agree within a percent or two for all three materials. The small differences between these two quantities have their origin in the implicit assumption of Born–von Karman cyclic boundary conditions when evaluating $\Delta \tilde{E}_v^u$. This gives rise to an interaction between the vacancy and its images, a spurious effect which is of the order of N^{-1} where N is the number of particles in the box. The good agreement between ΔE_v^u and $\Delta \tilde{E}_v^u$ provides a good check on our procedures as well as illustrating a practical use of $V_{\rm eff}(r)$.

The relaxation energy ΔE_v^r, calculated in the manner described in the previous section, will also have an N^{-1} correction which might be relatively larger than for $\Delta \tilde{E}_v^u$. However, as the results of table 1 show, ΔE_v^r is $\sim 15\%$ of ΔE_v^u and hence such corrections are not important. However, in the case of interstitials with much larger relaxations the situation could be different.

For each material, results are presented for $\Delta E_v = \Delta E_v^u + \Delta E_v^r$ at two different lattice parameters, one corresponding to low temperature and the other to the melting point. In each case ΔE_v decreases sharply with increasing lattice parameter. However, to make a comparison with experiment we must add to ΔE_v the entropy term Δ to give the formation enthalpy at constant pressure ΔH_p. These results are also given

Table 1. Vacancy formation energies (in electron volts) at constant volume for Li, Na and K plus experimental values for the lattice parameter a, thermal expansion coefficient α_p and compressibility K_T. ΔE^u and $\Delta \tilde{E}_v^u$ are the static unrelaxed values obtained, respectively, by summing equation (1.2) over the infinite lattice and by evaluating the energy per particle of an array of boxes, each originally of side $4a$ but with one particle removed and the box dimensions squeezed to maintain the condition of constant volume. ΔE_v^r is the relaxation energy of the squeezed lattice. $\Delta E_v \equiv \Delta E_v^u + \Delta E_v^r$. The formation enthalpy at constant pressure $\Delta H_p = \Delta E_v + \Delta$ where $\Delta = - T\alpha_p \Omega \Delta p_v$. The formation volume $\Delta \Omega_p$ is obtained from equation (A1.7).

Metal	T(K)	a(Å)	ΔE_v^u	$\Delta \tilde{E}_v^u$	$-\Delta E_v^r$	ΔE_v	Δ	ΔH_p	$\Delta \Omega_p/\Omega_0$	$\alpha_p(10^{-4} \, \text{K}^{-1})$	$K_T(10^{-11} \, \text{cm}^2/\text{dyn})$
Li	0	3·483	0·526	0·519	0·081	0·445	0	0·445	0·43		0·73[a]
Li	454	3·538	0·456	0·451	0·058	0·398	0·087	0·485	0·68	1·96[b]	0·95[a]
Na	0	4·225	0·292	0·293	0·040	0·252	0	0·252	0·65		1·27[c]
Na	371	4·309	0·213	0·218	0·025	0·188	0·108	0·295	0·72	2·27[e]	1·73[d]
K	0	5·233	0·340	0·343	0·050	0·290	0	0·290	0·59		2·70[f]
K	337	5·343	0·257	0·259	0·030	0·227	0·085	0·312	0·71	2·55[f]	3·34[f]

[a] Extrapolated from Nash and Smith (1959) and thermodynamic data quoted therein; [b] Beg and Nielsen (1976); [c] Extrapolated from Martinson (1969); [d] Fritsch *et al* (1973); [e] Adlhart *et al* (1975); [f] Schouten and Swensson (1974).

in table 1. It is most interesting to note that this additional term completely cancels the behaviour of ΔE_v with lattice parameter. The net result is a much weaker variation of ΔH_p. For Li and K the change in ΔH_p, as T goes from 0 to T_m, is less than 10%, although for Na it is a little larger, Most important, the change is positive as it should be. These findings seem to be more or less in accord with those of Leung and Stott (1977) who, using a different approach, concluded that vacancy formation energies in Na and Al are independent of temperature.

Finally we display in table 1 our calculated values of the formation volumes at constant pressure $\Delta \Omega_p$. For Na and K these quantities are very similar, being ~ 0.6 to $0.7 \, \Omega_0$, where Ω_0 is the atomic volume, and they exhibit only a small variation with temperature. On the other hand $\Delta \Omega_p$ is somewhat smaller at $T = 0$ for Li ($0.43 \, \Omega_0$), and increases by more than 50% to about the same value as for Na and K at $T = T_m$.

4. Comparison with experiment

4.1. Vacancy formation energy

Experimental values of the vacancy activation energy Q obtained in self-diffusion experiments are very accurate for Li (Ott and Lodding 1968), Na (Mundy 1971) and K (Mundy *et al* 1971). They are actually sufficiently accurate that the curvatures of respective Arrhenius plots have been well established for Na and K (and excluded for Li).

Formation energy measurements are generally much less precise and reproducible. Different methods, such as resistivity, specific heat and lattice spacings against volume expansion, do not agree as well as activation data determined from self-diffusion, creep or electromigration and thermal transport of defects.

Furthermore, the available formation energy data seem unsatisfactory in other respects. They do not correlate with the melting temperature of the metal, as Q does; when combined with Q they indicate a proportion of the formation and migration contribution to Q that varies considerably in the three alkali metals, as shown in table 2, and that is difficult to merge with other experimental results, like the heat of transport of the Soret effect for Na (Sullivan 1967).

Table 2. Experimental values of the vacancy activation energy Q and formation energy ΔE. Energies are in electron volts. For each metal T_m is the melting temperature. The values listed in the columns without temperature headings are, in the case of Q, for an intermediate temperature and, in the case of E_F, an average value over the measured temperature range.

	Li			Na			K		
T	0		T_m	0		T_m	0		T_m
Q	0.55[a]	0.56[h]	0.55[a]	0.37[c]	0.42[d]	0.45[c]	0.38[c]	0.42[f]	0.42[e]
E_f		0.34[g]			0.36[h]			0.39[i]	

[a] Ott and Lodding (1968); [b] Thernquist and Lodding (1968); [c] Mundy (1971); [d] Sullivan (1967); [e] Mundy *et al* (1971); [f] Kohler and Ruoff (1967); [g] Feder (1970); [h] Adlhart *et al* (1975); [i] MacDonald (1953).

The difficulty in correlating formation energies with the respective activation values and with the existing theoretical evaluation of the parameters of monovacancy diffusion has favoured interpretations of the experimental results that rely upon two or more defect types. This trend, strongly supported by the curvature exhibited by the Arrhenius plot of various metals (e.g. Na and K), has profited from the fact that calculations of formation and migration entropies are difficult and rare. This fact leaves a certain amount of freedom to postulate nonvanishing relative contributions of different defect types.

On the other hand, a glance at table 3 shows that the present results for the vacancy formation enthalpies (ΔH_p) of the three alkali metals correlate quite well with the activation energies. Taking the difference between these two quantities in each case yields our expected vacancy migration energy (ΔE_m) if only monovacancies contribute to the diffusion process. Note that these values, given in the third row of table 3, are rather similar for each element. Also note that they agree very well with the vacancy migration energies (ΔE_d^m) calculated by Schober $et\ al$ (1975) for Li and by Da Fano and Jacucci (1977) for Na and K using the same interionic potentials. These are shown in the fourth row of table 3.

Table 3. Comparison of vacancy migration energies ΔE_m, expected from the difference of the measured activation energies Q and the computed formation energies ΔE_v, with the values (ΔE_m^d) reported in the dynamical simulation study of the same model system by Da Fano and Jacucci (1977) for Na and K and for Li by Schober $et\ al$ (1974)

	Li		Na		K	
T	0	T_m	0	T_m	0	T_m
Q	0·55	0·55	0·37	0·45	0·38	0·42
ΔE_v	0·44	0·48	0·25	0·29	0·29	0·31
ΔE_m	0·11	0·07	0·12	0·16	0·09	0·11
ΔE_m^d	0·11		0·12	0·18	0·09	0·12

Dynamical simulation studies of the monovacancy migration were carried out by Da Fano and Jacucci (1977) in Na and K, using the molecular dynamics technique. Migration energies were obtained from jump frequencies and particle diffusion rates in runs corresponding to different temperatures in the range $T/T_m = (0.9–1.0)$, each including about 500 vacancy jumps. Different jump processes were observed to occur in their study:

(i) single jumps of the vacancy to a nearest neighbour site;
(ii) collinear double jumps of the vacancy;
(iii) single jumps of the vacancy to a second nearest neighbour.

The second and third mechanisms do not operate at $T = 0.9\ T_m$; they exhibit a migration energy about four times larger than single nearest neighbour jumps. At $T = T_m$ the double jumps contribute more than one-fourth of the vacancy displacements in Na and about one-sixth in K, while second-nearest-neighbour jumps contribute about 4% and 1% respectively. The values indicated in table 3 for $T = 0$ correspond to the migration energy exhibited (at high temperature) by the contribution to the diffusion coefficient of the single nearest-neighbour jumps taken separately, while at $T = T_m$ the values correspond to the total diffusion process.

No dynamical simulations of diffusion have been carried out for Li. However, Schober *et al* (1975) performed a static calculation using the same DRT potential as employed in this work and we have included their value of ΔE_m^d in table 3 as an indication of what a dynamical simulation can reasonably be expected to produce.

The extremely good, detailed agreement exhibited by the last two rows of table 3 leaves no room, in our opinion, for the contribution of a second defect type to diffusion in these metals. Note that Da Fano and Jacucci (1977) show that the mono-vacancy double jumps explain the anomalous decrease of the isotope effect found by Mundy in Na in the temperature range $T/T_m = (0.9-1.0)$, i.e. the strongest evidence for the contribution of more than one diffusion channel in Na.

The values of the formation energies calculated in the present work are not in agreement with the experimental values of table 2, and this remains an unsolved problem for the time being. It is perhaps appropriate to note here that the theoretical treatment employed to extract formation energies from dilatometric experiments is based on a theorem (Feder and Nowick 1958) arising from the work of Eshelby (1954) proven in the harmonic approximation only. It is then assumed that the effect of anharmonicity on the vacancy and lattice expansion is exactly the same in both cases, an assumption which in our opinion warrants further investigation.

Preliminary calculations on interstitial atoms and divacancies performed along the lines of the present work predict for Na a formation energy of the interstitial greater than half an electron volt and a negligible divacancy binding energy. Although these results indicate already that these types of defects should play a very minor role in self-diffusion and defect concentration measurements, accurate calculations of defect entropies would be very important to settle the matter in a definitive way.

4.2. Vacancy formation volume

In table 4 the calculated values $\Delta\Omega_p$ of the vacancy formation volume are compared to the experimental values of the activation volumes $\Delta\Omega_a$. The values for Na are obtained from Mundy's pressure experiment, interpreting the data with a single-defect type model. The value for K is reported in room temperature creep work (Kohler and Ruoff 1967) in which the activation energy for diffusion was found to be 0.42 eV, in good agreement with that found later in the self-diffusion experiment by Mundy. For all three materials, $\Delta\Omega_p$ is somewhat larger than $\Delta\Omega_a$. In view of the results obtained by Finnis and Sachdev (1976) we cannot reasonably expect much better agreement with experiment.

Note that, through equation (A.6), the entropic term in ΔH_p (Δ in table 1) is proportional to $\Delta\Omega_p$. Thus it might be argued that we have overestimated this term

Table 4. Comparison of the computed vacancy formation volumes $\Delta\Omega_p$ with measured activation volumes $\Delta\Omega_a$.

	Li		Na		K	
T	0	T_m	0	T_m	0	T_m
$\Delta\Omega_p/\Omega_0$	0.43	0.68	0.65	0.72	0.59	0.71
$\Delta\Omega_a/\Omega_0$		0.28[a]	0.48[b]	0.54[b]		0.55[c]

[a] Hultsch and Barnes (1962); [b] deduced from data of Mundy (1971) assuming a single defect mechanism; [c] Kohler and Ruoff (1967).

by, say, 30% at $T = T_m$. This would mean that our calculated values of ΔH_p at $T = T_m$ should be lowered by about 0·02 eV in each case, reducing the temperature dependence of this quantity and slightly improving the already very good agreement between the last two rows of table 3.

5. Comparison with another calculation

There are three features of our lattice statics calculation which make it superior to previous work. First of all we have correctly summed to convergence the long-range part of the interionic potential for the relaxed vacancy. A short-range cut-off can bring about serious errors when evaluating the energy in the squeezed lattice since this procedure is equivalent to evaluating the virial sums of equation (1.2) over the relaxed positions. Judicious selection of a truncation point can bring about sensible looking answers, but not necessarily ones in which confidence can be placed. Secondly the relaxed configurations are obtained with a computational method appropriate to a disordered system. Anharmonic effects in the relaxation process from the perfect lattice positions are taken into account automatically. Finally the pseudopotential description is of a completely fundamental nature with no adjustable parameters determined by experimental constraints. Also we have employed what we believe to be the best choice of dielectric function for this problem†.

Table 5. A comparison of our calculated formation energies ΔE(JT) and volumes $\Delta\Omega$ (this work: JT) with those of Ho, ΔE(Ho), $\Delta\Omega$(Ho) and with experimental quantities. All energies are in electron volts.

	Li	Na	K
T_m(K)	454	371	37
Q_{exp}	0·55–0·55	0·37–0·45	0·38–0·42
ΔE(Ho)	0·37	0·39(0·27)	0·36
ΔE(JT)	0·44–0·48	0·25–0·29	0·29–0·31
$(\Delta\Omega/\Omega_0)$(exp)	0·28	0·48–0·54	0·55
$(\Delta\Omega/\Omega_0)$(Ho)	0·53	0·54(0·71)	0·53
$(\Delta\Omega/\Omega_0)$(JT)	0·43–0·68	0·65–0·72	0·59–0·71

In addition to these comments on the lattice statics calculation, we point out that the entropy of formation has also been included and this allows us to extend our results to finite temperature. Because we feel that all these improvements are necessary to obtain a consistent picture of vacancy formation, we should compare with earlier calculations. A comprehensive review of earlier work is out of the question here and consequently we have chosen to make a comparison with one particular set of results which is fairly typical of earlier work, i.e. that of Ho (1971, 1973). In table 5 we compare our calculated formation energies and volumes with those of Ho along with some relevant experimental quantities. The most striking difference between the two calculations is that Ho's results are almost identical for the three metals, exhibiting no correlation either with the melting temperatures and measured self-diffusion energies in the case of ΔE or with the measured formation volumes in the case of $\Delta\Omega$. On the other hand our results show this correlation explicitly

†See Dharma-Wardana (1976) for a useful analysis of dielectric functions.

as well as the correct temperature dependence of the energies. We note that Ho's Na vacancy energy drops to a value in agreement with ours when the same screening (Geldart and Taylor 1970) is used. But the vastly different behaviour of the calculated Li results relative to Na and K almost certainly arises from the fact that Ho used only local pseudopotentials for his calculations whilst the DRT pseudopotentials are explicitly nonlocal, nonlocality being a very important feature of a good description of Li.

6. Conclusions

The present calculations of the vacancy formation energy in Li, Na and K, complemented by the vacancy migration study of Da Fano and Jacucci (1977) in Na and K yield an accurate and overall consistent picture of the properties of this point defect in these alkali metals. Extremely good agreement is found with the accurate measurements of the temperature-dependent activation energy for self-diffusion; the experimental and computed energies and the respective temperature dependences correlate with great precision and show the same variations from one element to another. On the other hand the computed formation energies do not agree particularly well with the measured values. This leads us to conclude that, either a fortuitous cancellation of errors has occurred between the Da Fano and Jacucci (1977) calculations and our results, or the experiments measuring formation energies need further interpretation. Keeping in mind that both the migration and formation energy calculations have used the same input data and that there were no adjustable parameters in either case, the first possibility seems rather unlikely. We therefore suggest that the question of the effect of anharmonicity on the interpretation of dilatation experiments should be re-examined with some care.

Accepting the good agreement with self-diffusion data, four conclusions follow naturally from these findings:

(i) there is no room for the contribution of a second defect type to the experimental results;

(ii) the DRT pair potentials give very accurate results for the alkali metals and three-body effects appear to be very small;

(iii) the dynamical anharmonic effects (other than the ones included in the quasi-harmonic description) are small even close to the melting point;

(iv) the explicit inclusion of the entropy increase, upon volume expansion, in forming the defect, is essential to obtain the correct values of formation energies at finite temperatures.

From our results it is clear that the curvature of Arrhenius plots of Na and K, and probably many others, can be ascribed to the temperature dependence of formation and migration parameters for a single defect mechanism, i.e. $-\partial D(T)/\partial(1/k_B T) = Q(T)$. This point of view has been repeatedly set forward, though never in a conclusive way because of the lack of accurate and reliable calculations of the T dependence of the parameters. Recently Gilder and Lazarus (1975) have espoused the same viewpoint but have suggested that the T dependence of Q is related to the T dependence of the vacancy formation volume. In particular they predict a strong curvature for those metals where the defect exhibits an expansivity much higher than the crystal itself. Unfortunately our model calculation does not

show this correlation. It is not clear why this should be so and this is a question that should be resolved in the near future.

Acknowledgments

Appendix 1

This Appendix is dedicated to the derivation of an expression for the vacancy formation enthalpy that is particularly suited for use in a quasiharmonic approximation scheme for metallic model systems based on the pseudopotential description. The expression is equally valid for migration enthalpy.

We start by recalling the well known equality of constant-pressure defect Gibbs free energy and constant-volume Helmholtz free energy. The defect affects the lattice properties to order $1/N$, i.e. to the order of its concentration in the crystal, so we can consider linear terms in Taylor expansions. Let us focus on an isothermal variation of the Gibbs free energy of a crystal in thermodynamic equilibrium conditions. Since at equilibrium $(\partial G/\partial \Omega)_T = 0$ and $(\partial G/\partial P)_T = \Omega$, the differential of G at constant T is

$$dG = \Omega \, dP. \tag{A1.1}$$

If we now use this result to relate Gibbs free energies of formation at constant pressure and constant volume, we have

$$\Delta G_v = \Delta G_p + \Omega \Delta P \tag{A1.2}$$

if ΔP is the pressure increase in forming the defect at constant volume. On the other hand, the relation $G = F + P\Omega$ gives

$$\Delta G_v = \Delta F_v + \Omega \Delta P \tag{A1.3}$$

From equations (A1.2) and (A1.3) we get the important result

$$\Delta G_p = \Delta F_v \tag{A1.4}$$

which can be explicitly written as

$$\Delta U_p - T\Delta S_p + P\Delta \Omega_p = \Delta U_v - T\Delta S_v.$$

Note that $\Delta \Omega_p$ is the formation volume at constant pressure and that $\Delta \Omega_p/\Omega_0 = 1 + \Delta \Omega_r/\Omega_0$ where $\Delta \Omega_r$ is the relaxation volume (usually negative). The formation enthalpy at constant pressure is then;

$$\Delta H_p = \Delta U_p + P\Delta \Omega_p = \Delta U_v + T(\Delta S_p - \Delta S_v). \tag{A1.5}$$

The last term in equation (A1.5) is determined by the entropy increase upon expansion by $\Delta \Omega_p$, of the lattice containing the defect. It can be evaluated as $T(\partial S/\partial \Omega)_T \Delta \Omega_p$

using the perfect crystal values of the thermodynamic derivative.

$$\left(\frac{\partial S}{\partial \Omega}\right)_T = \left(\frac{\partial P}{\partial T}\right)_\Omega = -\left(\frac{\partial \Omega}{\partial T}\right)_P \left(\frac{\partial P}{\partial \Omega}\right)_T = +\left|\frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial T}\right)_P\right| \Big/ \left[-\frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial P}\right)_T\right] = \alpha_p/K_T$$

where α_p is the lattice expansivity and K_T the isothermal compressibility. We shall then rewrite equation (A1.5) as

$$\Delta H_p = \Delta U_p + T(\alpha_p/K_T)\Delta\Omega_p. \tag{A1.6}$$

In a constant-volume calculation of the formation parameters, $\Delta\Omega_p$ can be evaluated through the pressure increase ΔP_v upon formation of the defect at constant volume, making use of the compressibility of the crystal:

$$\Delta\Omega_p = -\Omega K_T \Delta P_v. \tag{A1.7}$$

Substituting in equation (A1.6) we find

$$\Delta H_p = \Delta U_v - T\alpha_p\Omega\Delta P_v. \tag{A1.8}$$

In the quasiharmonic static approximation, the pressure is evaluated as

$$-\frac{\partial E}{\partial \Omega} = -\left(\frac{\partial E_j(\Omega)}{\partial \Omega}\right) - \left(\frac{\partial}{\partial \Omega}\right)\left\{\frac{1}{2}\sum_l{}' V(r_l,\Omega)\right\} - \frac{1}{6\Omega}\sum_l{}' r_l\left(\frac{\partial V}{\partial r_l}\right)(r_l,\Omega).$$

Upon taking constant volume difference, the first term in this expression cancels out exactly and the quantities ΔU_v and ΔP_v are then easily evaluated in a static calculation from energy sums and virial sums of ionic pair interactions relative to the defect and perfect crystals having identical lattice parameters. The temperature dependence then enters the expression in equation (A1.8) through the variation with temperature of the lattice spacing and of its temperature derivative. It turns out that the two terms on the right-hand side of equation (A1.8) have an opposite temperature variation that largely compensates in their algebraic sum ΔH_p. Since the second term overcomes the first, neglecting it results in the prediction of the wrong sign for the temperature dependence of ΔH_p.

Appendix 2

The relaxation energies quoted in connection with the vacancy formation and migration are obtained from computations in which the structure of the system is allowed to relax at constant volume to the configuration of energy minimum. The search for the energy minimum is done in a standard way with the help of a modified molecular dynamics program. At every integration time step all particle velocity components having opposite sign with respect to the relative component of the resultant force on the particle are equated to zero.

In this way the system is allowed to evolve downhill in potential energy under the effect of the interaction forces. The kinetic energy that thus develops is extracted from the various degrees of freedom when the respective coordinate overshoots the bottom of the valley and starts climbing uphill again. This method is rather efficient and perfectly adequate for this purpose.

The system evolves in our case for some one or two hundred steps. The total internal energies rapidly stabilise in the seventh or eighth figure and coincide within this accuracy with the total energy—the effect to be read off is of the order of $1/N$, so that this precision is more than adequate with a few hundred particles.

Note Added in Proof. Our attention has been drawn to a paper by A V Chadwick and H R Glyde in *Rare Gas Solids*, volume II edited by M L Klein and J A Venables (Academic Press 1977), page 1151. These authors have also stressed the importance of anharmonic effects in the temperature-dependent vacancy formation enthalpy and have derived independently our equation (A1.6). See their equation (2.36).

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