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Ab initio calculation of formation and migration volumes for vacancies in Li and Na

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The formation, migration, and activation volumes for monovacancies in Li and Na for zero and finite external pressure are calculated *ab initio* within the framework of the local-density approximation and the *ab initio* pseudopotential method. In both materials the activation volumes are smaller than half of the atomic volume. The approximations involved in the transition-state theory which is the basis for the calculations are discussed with special emphasis on the limitations of the theory at very high pressure. The results are compared with experimental data on self-diffusion. [S0163-1829(97)04509-8]

I. INTRODUCTION

It appears to be widely accepted that monovacancies play an important role for self-diffusion in bcc Li and Na. In both materials the simultaneous measurements of thermal expansion and of lattice parameters have shown[1–3] that vacancies and not self-interstitials are the dominant atomic defects in thermal equilibrium (self-interstitials could be also excluded by *ab initio* calculations[4,5] due to the high formation energies). For the case of Na the atomic jump processes were studied[6] by means of quasielastic neutron scattering and it was concluded that self-diffusion in Na is due to random migration of monovacancies and divacancies. Finally, the activation energy for self-diffusion via monovacancies in Li obtained[7,8] by the *ab initio* electron theory agreed very well with the experimental activation energy for self-diffusion[9,10] at least for not too small temperatures, and for Na the corresponding *ab initio* result[8] agreed very well with the smallest activation energy obtained by fitting the experimental data[11,12] from a wide temperature range by two or three exponentials. Nevertheless, there are some peculiarities which are still under discussion:

(i) Most recently an additional very small activation energy was found by ^{24}Na tracer experiments[13] below 200 K.

(ii) In both materials the migration energies E_{1V}^{m} obtained by *ab initio* calculations within the framework of the transition-state theory[14] are very small [0.055 ± 0.01 eV for Li, (Refs. 7 and 8) and 0.054 ± 0.01 eV for Na (Ref. 8)]. While such low values are compatible with the data obtained[15] from experimental phonon dispersion curves, it may be argued[16] that for $E_{1V}^{m}/k_BT \lesssim 3$ (which applies to the high-temperature experiments in Li and Na) the notion of discrete jumps is no longer valid and the transition-state theory should fail. However, it has been demonstrated by molecular-dynamics simulations for Na (Ref. 17) and for Zr (Ref. 18) that even in the case of low migration energies the ‘‘static migration energy’’ obtained by the transition-state theory agrees well with the ‘‘dynamical migration energy’’ obtained from the temperature dependence of the vacancy diffusivity in the molecular-dynamics simulations.

(iii) The kinetic energy factor ΔK obtained experimentally[11] from the isotope-effect parameter is 0.52 for the case of Na which means that only half of the translational kinetic energy of the system may be attributed to the jumping atom when it crosses the saddle point. Although this does not strictly exclude the monovacancy mechanism it was noted that low kinetic form factors would naturally arise for a self-diffusion mechanism by direct exchange of adjacent atoms. However, *ab initio* calculations[8] yielded activation energies for the direct exchange in Li and Na which are about a factor of 3 larger than the experimental activation energies for self-diffusion.

(iv) The experimental activation volumes V^{SD} obtained from the pressure dependence of the self-diffusion constant D^{SD} according to

$$V^{\mathrm{SD}} = -k_BT\partial \ln D^{\mathrm{SD}}/\partial p|_T \tag{1}$$

are rather small. For Li Hultsch and Barnes[19] found $V^{\mathrm{SD}} = 0.28\ \Omega_0$ (Ω_0 = atomic volume) for temperatures between 310 and 350 K and pressures up to 0.7 GPa, whereas Mundy[11] obtained for Na for the above-mentioned process with the smallest activation energy an activation volume of $0.32\ \Omega_0$ for temperatures larger than 288 K and pressures up to 0.95 GPa. It was noted[16] that for a monovacancy mechanism such low activation volumes would be surprising, albeit the monovacancy mechanism cannot be excluded by these results. Recent measurements of the NMR linewidth[20,21] at room temperature and pressures up to 5 GPa indicate a decrease of the activation volume with increasing pressure, arriving at values of $0.1\ \Omega_0$ for Li and $0.175\ \Omega_0$ for Na at the highest available pressures. The question arises whether this pressure dependence of the activation volume results from the superposition of two or more diffusion mechanisms and a suppression with increasing pressure of those mechanisms with large activation volume, or whether it originates from an intrinsic pressure dependence of V^{SD} for one mechanism.

In the present paper the activation volumes for self-diffusion via monovacancies in Li and Na are calculated by the ab-initio electron theory to investigate whether such low activation volumes are possible for monovacancies and whether they exhibit an intrinsic pressure dependence.

II. THE TRANSITION-STATE THEORY FOR THE ACTIVATION VOLUME

In this section we report on the results of the transition-state theory[14,22] for the activation volume of self-diffusion

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via monovacancies. Comments on the various assumptions involved are given in the Appendix. It should be noted that the transition-state theory is formulated within the framework of classical statistical mechanics. We therefore exclude quantum effects of diffusion from the very beginning. This is certainly justified for Na, whereas for Li a contribution of quantum effects cannot be ruled out strictly.

For the case of a defect mechanism the self-diffusion constant D^{SD} entering Eq. (1) may be written as

$$D^{\mathrm{SD}}=ga^2c^{\mathrm{eq}}\Gamma, \tag{2}$$

where g is a geometrical factor, a the lattice constant, c^{eq} is the concentration of the defect in thermal equilibrium, and Γ denotes the jump rate of the defect. Both c^{eq} and Γ may be obtained in principle from molecular dynamics simulations, the concentration via a thermodynamic integration method for the calculation of the formation free enthalpy,[23] and the jump rate from the mean-square displacement of the atoms. Such calculations may be performed based on pair potentials[17,18] or by the use of *ab initio* techniques (for instance, Smargiassi and Madden[24] have developed an orbital-free *ab initio* molecular dynamics method for Na). We will use an alternative method for which all quantities may be obtained by static calculations and which is based on the transition-state theory for the determination of the jump rates. This transition-state theory involves several assumptions and approximations which may be criticized, especially at high external pressure (see Appendix). On the other hand, it provides a simple physical picture of the complex dynamical process of vacancy migration and a powerful computational tool which requires much less computational effort than molecular dynamics simulation. In principle, of course, the latter method can be used to check the predictions of the transition-state theory if there is enough computer time to obtain the required statistical accuracy, and indeed several aspects of the transition-state theory have already been tested by molecular dynamics simulations based on pair-potentials.[17,18] In the following we will describe in detail our static calculational method based on the transition-state theory.

For a monovacancy the concentration is given by

$$c^{\mathrm{eq}}_{1V}=e^{S^f_{1V}/k_B}e^{-H^f_{1V}/k_BT}. \tag{3}$$

Here S^f_{1V} and H^f_{1V} denote the formation entropy and the formation enthalpy, respectively, which describe the change in entropy and enthalpy when a vacancy is formed, i.e., when an atom is removed from a regular lattice site and inserted at a typical surface site (''Halbkristall-Lage''), with

$$H^f_{1V}=E^f_{1V}+pV^f_{1V}. \tag{4}$$

The quantity E^f_{1V} is the vacancy formation energy, and V^f_{1V} denotes the monovacancy formation volume which is composed of the change in volume ΔV^f_{1V} upon total removal of one atom from the system and the atomic volume Ω_0 gained when inserting the atom at the typical surface site,

$$V^f_{1V}=\Delta V^f_{1V}+\Omega_0. \tag{5}$$

Within the assumptions of the transition-state theory of defect migration[14,22] (see Appendix) a prescription is given how to calculate the jump rate Γ, arriving at

$$\Gamma=\prod_{j=1}^{3n-6}\nu_j(\tilde{V}^i)/\prod_{j=1}^{3n-7}\nu'_j(\tilde{V}^s)\exp(-H^m_{1V}/k_BT). \tag{6}$$

Here the ν_j denote the vibrational frequencies for the system with the vacancy associated to the initial lattice site (i), $\tilde{V}^i$ is the equilibrium volume for this state at given temperature T and pressure p, and n is the number of atoms. The ν'_j are the vibrational frequencies of the system around the saddle point (s), i.e., with the jumping atom confined to the ridge of the potential energy ϕ separating the initial and the final state of the jump and with the motion of the atom along the coordinate responsible for the instability of the saddle point being prevented. $\tilde{V}^s$ is the equilibrium volume for this state and given p, T. The migration enthalpy H^m_{1V} is given by

$$H^m_{1V}=E^m_{1V}+pV^m_{1V}, \tag{7}$$

with the migration energy

$$E^m_{1V}=\phi(\tilde{V}^s)-\phi(\tilde{V}^i) \tag{8}$$

and the migration volume

$$V^m_{1V}=\tilde{V}^s-\tilde{V}^i. \tag{9}$$

Flynn[22] has rewritten Eq. (6) in a form more keeping with the way experimental analyses are presented,

$$\Gamma=\nu_oe^{S^m_{1V}/k_B}e^{-H^m_{1V}/k_BT}. \tag{10}$$

Here ν_o is an arbitrary frequency (usually taken as the Debye frequency) and the quantity

$$S^m_{1V}=k_B\ln\left[\prod_{j=1}^{3n-6}\nu_j(\tilde{V}^i)/\left(\nu_0\prod_{j=1}^{3n-7}\nu'_j(\tilde{V}^s)\right)\right] \tag{11}$$

is called migration entropy. Altogether, D^{SD} is given by

$$D^{\mathrm{SD}}=ga^2\nu_0e^{-G^{\mathrm{SD}}_{1V,p}/k_BT} \tag{12}$$

with the free enthalpy of activation at constant pressure

$$G^{\mathrm{SD}}_{1V,p}=G^f_{1V,p}+G^m_{1V,p}=E^f_{1V}+pV^f_{1V}-TS^f_{1V}+E^m_{1V}+pV^m_{1V}-TS^m_{1V}. \tag{13}$$

The activation volume for self-diffusion via monovacancies as obtained from Eqs. (1), (12), and (13) is

$$V^{\mathrm{SD}}_{1V}=\frac{\partial G^{\mathrm{SD}}_{1V,p}}{\partial p}=\frac{\partial G^f_{1V,p}}{\partial p}+\frac{\partial G^m_{1V,p}}{\partial p}=V^f_{1V}+V^m_{1V}. \tag{14}$$

Obviously, the formation and migration volume defined formally via

$$V^f_{1V}=-k_BT\frac{\partial\ln c^{\mathrm{eq}}_{1V}}{\partial p}\Big|_T \tag{15}$$

and

$$V_{1V}^{m}=-k_BT\frac{\partial\ln\Gamma}{\partial p}|_T \tag{16}$$

have indeed the simple physical meaning of the change in system volume upon formation and migration of the vacancy, respectively. (In compounds the situation is much more complicated; see Ref. 25.) However, it becomes clear from the Appendix that this holds only for not too large pressures p, i.e., $p/B\ll 1$, where B denotes the bulk modulus. For larger pressures the situation is much more complicated and the formation and migration volume defined via Eqs. (15) and (16) no longer have a simple geometrical meaning. In the high-pressure experiments of Refs. 20 and 21 we have for $p=5$ GPa the ratio $p/B\approx 0.4$ (0.7) for Li (Na). Therefore, the comparison of these experimental results with theoretical data from calculations based on the above formulae is critical. In our calculations of Sec. IV we confine ourselves to smaller pressures, i.e., 3.4 GPa (2.8 GPa) for Li (Na) with $p/B\approx 0.3$ (0.4).

III. CALCULATIONAL PROCEDURE

The calculations are performed within a supercell formalism, i.e., large supercells containing N sites and one vacancy, respectively, are periodically arranged. For infinitely large supercells the properties of an isolated vacancy are approached. Because in the calculations finite supercell sizes are used, the results have to be checked for convergence with respect to the supercell size.

Within the supercell formalism the vacancy formation and migration energy may be written as

$$E_{1V}^{f}=E(N-1,1,\Omega_{1V})-E(N,\mathrm{O},\Omega)+\frac{1}{N}E(N,\mathrm{O},\Omega_{1V}), \tag{17}$$

$$E_{1V}^{m}=E^{s}(N-1,1,\Omega_{1V}^{s})-E(N-1,1,\Omega_{1V}). \tag{18}$$

Here $E(N-1,1,\Omega_{1V})$ is the energy of a supercell at the volume Ω_{1V} containing $N-1$ atoms and one vacancy. $E(N,O,\Omega)$ is the energy of a perfect supercell with volume $\Omega=N\Omega_0$, and the last term of Eq. (17) accounts for the energy gain due to the insertion of the atom at a typical surface site. Accordingly, $E^{s}(N-1,1,\Omega_{1V}^{s})$ is the energy of the supercell containing $N-1$ atoms, thereby one atom in the saddle point s, and Ω_{1V}^{s} is the volume of the supercell for this configuration. The volumes Ω,Ω_{1V}, and Ω_{1V}^{s} have to be chosen according to the constraints prescribed for the vacancy formation. For instance, *for zero temperature and zero pressure* they correspond to their equilibrium volumes obtained directly from a two-step calculation. In the first step (‘‘structural relaxation’’) the supercell volume is kept constant, and the relaxations of the atomic positions is performed by moving the atoms around the vacancy or around the atom in the saddle point until the forces acting on the atoms are zero. In a second step (‘‘volume relaxation’’) the system is allowed to shrink or expand homogeneously until the total energy reaches its minimum. It turned out that the forces on the atoms which reappear after this second step are very small so that it is not necessary to perform again a structural relaxation. For the vacancy formation it has been shown (see Ref. 5, and references therein) that the change in the supercell volume obtained by the volume relaxation is equivalent to the change in volume ΔV_{1V}^{f} of a large but finite crystal with traction-free surfaces upon total removal of one atom from the system , i.e.,

$$\Delta V_{1V}^{f}=\Omega_{1V}-N\Omega_0. \tag{19}$$

As outlined in Sec. II, the vacancy formation volume then is given by $V_{1V}^{f}=\Delta V_{1V}^{f}+\Omega_0$. Accordingly, the vacancy migration volume for zero temperature and zero pressure may be obtained from the difference in the equilibrium volume of the system with the jumping atom on the one hand in the static, fully relaxed saddle point configuration, on the other hand in the static, fully relaxed initial configuration of the jump.

For nonzero temperature and nonzero pressure, however, the formation and migration volumes cannot be obtained by static relaxations. Instead, we use the first part of Eq. (14) and determine the volumes from the pressure derivatives of the free enthalpies of formation and migration,

$$V_{1V}^{f}=\frac{\partial G_{1V,p}^{f}}{\partial p},\quad V_{1V}^{m}=\frac{\partial G_{1V,p}^{m}}{\partial p}. \tag{20}$$

Equations (20) may be transformed[26,27] to relations more suitable to supercell calculations,

$$\frac{\partial G_{1V,p}^{f}}{\partial p}=\frac{\partial F_{1V,V}^{f}}{\partial p}=\frac{\partial F_{1V,V}^{f}}{\partial V}\frac{\partial V}{\partial p}, \tag{21}$$

$$\frac{\partial G_{1V,p}^{m}}{\partial p}=\frac{\partial F_{1V,V}^{m}}{\partial p}=\frac{\partial F_{1V,V}^{m}}{\partial V}\frac{\partial V}{\partial p}. \tag{22}$$

Here $F_{1V,V}^{f,m}$ are the free energies of formation and migration under the constraint of a fixed system volume, with

$$F_{1V,V}^{f,m}=E_{1V,V}^{f,m}-TS_{1V,V}^{f,m}. \tag{23}$$

Performing the vacancy formation at fixed system volume means that the lattice constant is reduced because the number of sites is increased by one due to the insertion of the atom at the surface. For the supercell calculations according to Eqs. (17),(18) this means

$$\Omega_{1V}=\frac{N}{N+1}\Omega,\quad \Omega_{1V}^{s}=\Omega_{1V}. \tag{24}$$

In the present paper we calculate the formation and migration volumes at zero temperature where there is no contribution of a pressure-dependence of the formation and migration entropies. This must be taken into account when comparing the results with experimental data which are performed at high temperatures. It has been shown by Harding[28] that for finite temperatures the formation volumes of Schottky defects in KCl are significantly overestimated when neglecting the entropy contributions. We therefore will calculate in future the entropy contribution to the vacancy formation volume in Na, based on the static calculation of force constants.[7] It turned out[7] that for Li the vacancy formation entropy could be reliably determined by the force constant method. We therefore think that it should also be possible to

TABLE I. Theoretical results (for $T = 0$ K) and experimental results (at finite temperature) for V^f_{1V}, V^m_{1V}, and V^{SD} in Li, in units of the atomic volume Ω_0 for a perfect Li crystal.

	This paper		experiment	
	$p = 0$	$p = 3.4$ GPa	Ref. 19 $310\ \mathrm{K} \leqslant T \leqslant 350$ K $0 \leqslant p \leqslant 0.7$ GPa	Ref. 21 $T = 300$ K $p = 4$ GPa
V^f_{1V}	0.49	0.36		
V^m_{1V}	-0.2	-0.06		
V^{SD}	0.29	0.30	0.28	0.1

TABLE II. Theoretical results (for $T = 0$ K) and experimental results (at finite temperature) for V^f_{1V}, V^m_{1V}, and V^{SD} in Na, in units of the atomic volume Ω_0 for a perfect Na crystal.

	$p = 0$	$p = 2.8$ GPa	Ref. 11	Ref. 21
			$T > 288$ K $0 < p < 0.95$ GPa	$T = 300$ K $p > 1$ GPa
V^f_{1V}	0.5	0.29		
V^m_{1V}	-0.01	-0.01		
V^{SD}	0.49	0.28	0.32	0.175

obtain its pressure dependence reliable for the case of Na. Altogether, it becomes obvious that our procedure allows to determine the activation volume even at finite temperatures by purely static calculations.

The calculations were performed within the framework of the local-density approximation and the *ab initio* pseudopotential theory (see Refs. 4,5 for the details of the pseudopotential constructions). The volume relaxation turned out to be numerically highly critical because the dependence of the total energy of the supercell on the volume is far from being smooth for realistic values of the energy-cutoff E_c, especially for the case of Li. This results from the fact that for fixed E_c the number of plane waves changes discontinuously when changing the system volume. To cope with this problem[29] we do not just consider the energy of a supercell containing the defect, but we substract the energy of a perfect supercell with the same number of sites, the same volume, the same energy-cutoff E_c and the same number of k points for the sampling of the Brillouin zone. It turned out that the difference in energies depends on the volume in a much smoother manner than the single energies when using the same E_c. The single energies of the supercells with the defect then are obtained by adding to these differences the energy of the corresponding perfect supercell which is obtained from a one-atom supercell calculation for an equivalent[5] set of k points but for much larger energy-cutoff E_c. For finite pressure the calculations are performed according to Eqs. (20)–(24). The derivatives $(\partial E^{f,m}_{1V,V})/(\partial V)$ thereby are approximated by $[E^{f,m}_{1V,V}(2)-E^{f,m}_{1V,V}(1)]/(V_2-V_1)$, i.e., they are determined by calculations for two volumes V_2 and V_1 with V_2-V_1 being reasonably small but not too small in order to avoid numerical problems. The derivative $(\partial V)/(\partial p)$ is obtained from the binding energy curve $E(V)$ of the perfect crystal via $p(V)=-\partial E(V)/\partial V$. To check this second type of calculation we have determined the vacancy formation volume of Na at zero pressure and temperature, once via the volume relaxation and once according to Eq. (20), and the results agreed well.

IV. RESULTS AND DISCUSSION

Tables I and II compile our results for the formation and migration volumes in Li and Na at zero pressure (from the volume relaxation) and at non-zero pressure [from Eqs. (20)–(24)] as obtained from supercells containing 54 sites. All calculations were performed for 4 Monkhorst-Pack[30] k points. For Li we used $E_c = 8.5$ Ry (16 Ry) for p = 0 (3.4 GPa), for Na we had $E_c = 9$ Ry for both pressures. In addition, we have performed calculations for a smaller supercell containing 16 sites with different sets of energy-cutoffs E_c and numbers of k points used for the sampling of the Brillouin zone. From these additional calculations we estimate that the possible error due to the use of a finite supercell size, a finite number of k points and a finite energy-cutoff E_c is about $\pm\ 0.05\ \Omega_0$. Of course, no estimate of the systematic error due to the use of the local-density approximation can be given.

We emphasize the following points:

(i) For zero pressure the vacancy formation volume is about 0.5 Ω_0 for Li and Na.

(ii) The migration volume is much smaller than the formation volume (especially for Na), in agreement with the general expectation. The migration volumes are negative both for Li and for Na. Of course the atoms next to the migrating atom in the saddle point configuration are pushed away and this would tend to enlarge the system volume, but this is obviously overcompensated by the relaxation of the further distant neighbors. However, we would not dare to argue that the migration volumes of all bcc metals should be negative.

(iii) The vacancy activation volume for Li at zero temperature and zero pressure is 0.29 Ω_0. This compares well to the experimentally obtained activation volume of 0.28 Ω_0 for finite temperature and low pressure.[19]

(iv) The vacancy activation volume for Na at zero temperature and zero pressure is 0.49 Ω_0. This is larger than the experimentally obtained[11] activation volume of 0.32 Ω_0 for $T > 288$ K and small pressure.

(v) The vacancy formation volume at zero temperature is drastically reduced by the application of a strong external pressure. For Na this yields a strong decrease of activation volume (because the migration volume remains very small), in qualitative agreement with the experimental observation. For Li the change in the formation volume is nearly compensated by a modification of the migration volume, so that the activation volume remains nearly constant, in contrast to the experimentally observed strong reduction.

To conclude, it has been demonstrated by *ab initio* calculations that at zero temperature the activation volumes for self-diffusion via vacancies are indeed smaller than 0.5 Ω_0. Furthermore, it appears that there is an intrinsic pressure dependence of the formation, migration, and activation volumes. There are quantitative discrepancies between the calculated zero-temperature vacancy activation volumes and the experimentally obtained finite-temperature activation volumes for self-diffusion. Part of these discrepancies may arise from the fact that there is an appreciable entropy contribution at finite temperatures which has been neglected in the zero-temperature calculations. For very large external pressures a further origin for the discrepancies may be the fact that the underlying formulae of the statistical mechanics (for instance, the transition-state theory) are no longer strictly valid. Finally, it must be recalled that the experimentally obtained pressure dependence of the activation volume could in principle also arise from the superposition of two or more diffusion mechanisms and a suppression with increasing pressure of those mechanisms with large activation volume.

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APPENDIX

In this appendix we make some comments on the transition-state theory. The key assumption of this theory is that for a calculation of the classical jump rate Γ of an atom it is not necessary to follow explicitly the trajectory of the atom, but it can be obtained by means of a statistical mechanics description in the configurational space spanned by the $3n$ coordinates and the $3n$ momenta of all the atoms in the system. This is of course a hypothesis because the probability distributions of statistical mechanics are constructed in such a way that they yield the correct thermal averages of thermodynamic variables, which does not guarantee that they yield also correct statistical results for dynamical variables (in addition, it should be noted that the distributions hold only for a coarse-grained scale in the configurational space). In spite of the resulting ample criticism on the transition-state theory[31,32] and the various extensions of the theory and the development of alternative theories[31] it is still successfully applied to describe diffusional properties in many systems.

If we prescribe in the experiment the pressure p rather than the volume V of the system, we have to supplement the configurational space by one more degree of freedom, i.e., by the volume of the system which may fluctuate in thermal equilibrium. The dynamics of the representative point of the system in the configurational space is determined by the Hamiltonian $H(\mathbf{p},\mathbf{q},V)$ consisting of a kinetic part $T(\mathbf{p})$ and a potential part $\phi(\mathbf{q},V)$. The initial state of the system before the jump is described by a small part i of the configurational space around a local minimum of the enthalpy $\phi(\mathbf{q},V)+pV$, for which the considered atom may be associated with one lattice site. The final state after the jump is characterized by a second part f around a local minimum of the enthalpy. The two minima are separated by a ridge of the enthalpy with an extremum at the saddle point s. The jump rate i to f then is defined as

$$\Gamma = j_s / n_i , \tag{A1}$$

where j_s is the flux of the representative point of the system from i to f over the ridge of the enthalpy and n_i is the probability that the system is in part i of the configurational space. The quantities j_s and n_i are calculated from integrals containing the probability to find the system in an interval of size $d^{3n}p\,d^{3n}q\,dV$ around $(\mathbf{p},\mathbf{q},V)$ given by

$$\begin{aligned}&\rho(\mathbf{p},\mathbf{q},V)\,d^{3n}p\,d^{3n}q\,dV\\ &\quad\sim \exp\left[-\frac{H(\mathbf{p},\mathbf{q},V)+pV}{k_BT}\right]d^{3n}p\,d^{3n}q\,dV.\end{aligned} \tag{A2}$$

For the integrations we first prescribe a volume, perform the integrations over the coordinates for fixed volume and finally the integrations over all volumes. Because the integrals are nearly exclusively determined by the parts i and s of the configuration space around the local extrema of the enthalpy we evaluate the enthalpy for small pressure according to

$$\begin{aligned}\phi(\mathbf{q},V)+pV &= \phi(V_0)+\frac{B}{2V_0}(V-V_0)^2\\ &\quad + pV + \frac{1}{2}\sum_i \omega_i^2(V)(q_i')^2\\ &= \phi(\tilde{V})+\frac{B}{2V_0}(V-\tilde{V})^2 + p\tilde{V}\\ &\quad + \frac{1}{2}\sum_i \omega_i^2(V)(q_i')^2.\end{aligned} \tag{A3}$$

Here V_0 is the equilibrium volume at $p=0$, B is the bulk modulus, the q_i' are normal coordinates, the $\omega_i(V)$ are the normal frequencies for the system at volume V, and

$$\tilde{V} = V_0\left(1-\frac{p}{B}\right) \tag{A4}$$

is the equilibrium volume at pressure p. Furthermore, we assume that for small pressure the frequencies depend linearly on the volume,

$$\omega_i(V)=\omega_i(V_0)\left[1-\frac{(V-V_0)}{V_0}\gamma_i\right]\approx\omega_i(\tilde{V}_0)\left[1-\frac{V-\tilde{V}_0}{V_0}\gamma_i\right], \tag{A5}$$

where the γ_i are Grüneisen's constants. With the approximations (A3)–(A5) the integrations required in the transition-state theory may be performed. Assuming in addition the same bulk modulus for the system in state i and s we arrive at Eqs. (7)–(11) of Sec. II. In contrast to the more heuristical derivation of these equations for finite pressure in Ref. 22, our present discussion demonstrates that these equations and the related geometrical interpretation of the formation volume defined formally via $V_{1V}^m = -k_BT(\partial \ln\Gamma)/(\partial p)|_T$ hold only for not too strong external pressure p. It should be noted that the approximations (A3)–(A5) must be performed also for the calculation of the vacancy concentration for finite p, so that the same remarks hold for the formation volume V_{1V}^f.

It is often argued that the results (7)–(11) of the transition-state theory (Sec. II) can only be valid if a quasiequilibrium state exists with the considered atom near the saddle-point configuration for a time scale much larger than the inverse Debye frequency, which is certainly unrealistic. As a consequence, it was argued that the real migration volume should be smaller than the one of the transition-state theory because during the rapid jump event the system is not able to develop the full static relaxation in the saddle point. The physical notion behind this criticism is that the system may be subdivided into the considered atom and the rest atoms, and that the considered atom initiates the lattice distortions during its rapid jump. Flynn[22] has outlined that this is not the correct interpretation of the transition-state theory: In this theory the jump process is related to collective fluctuations of the many-body system, the statistical weights of which are determined by Eq. (A2). The result (8) for the migration energy then simply means that only those configurations with low excitation energies contribute with statistical significance, whereas the other configurations are suppressed by the very rapidly decreasing exponential probability distribution. So as long as we believe in the transition state theory (which may be criticized, see above) there is no space for a time-scale argument.

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