First-Principles Calculations of Absolute Concentrations and Self-Diffusion Constants of Vacancies in Lithium

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For lithium the absolute concentrations of thermal monovacancies and the self-diffusion constants via vacancies are calculated *ab initio* using the local-density approximation in combination with the transition-state theory of diffusion. The diffusion data are in good agreement with experimental data for high temperatures. [S0031-9007(96)00663-1]

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The mechanisms of self-diffusion in solids have been intensively discussed for several decades (for reviews, see Refs. [1] and [2]). Possible candidates [1] are nondefect mechanisms such as the direct exchange of two atoms on adjacent lattice sites or ring mechanisms involving more than two atoms, and defect mechanisms via monovacancies, divacancies, or self-interstitials. Concerning elementary metals, the monovacancy mechanism is confirmed [1] to be dominant in fcc and hcp metals as well as in bcc Fe. In other bcc metals the situation is less clear, and the self-diffusion is sometimes, at least in part, influenced by the characteristic low-frequency LA $2/3\ \langle 111 \rangle$ phonon mode [3]. Solid Li in the bcc phase is especially intriguing because it possesses a rather "open" structure, i.e., a rather large lattice constant and low electron density. It was therefore suggested that, in addition to the monovacancy mechanism, there might be contributions of self-interstitials at high temperatures [4] and of direct exchange or extended ring mechanisms at low temperatures [1]. In the present Letter we report on parameter-free *ab initio* calculations of the self-diffusion parameters for these mechanisms in Li. For Si a similar study has been performed by Blöchl *et al.* [5] with the result that the self-interstitial mechanism is dominating over the contribution of the other mechanisms.

In a cubic crystal the tracer self-diffusion is described by the self-diffusion constant $D^T(T)$. Experimentally, it turns out that in many cases this quantity may be described by an Arrhenius behavior,

$$D^T(T) = D_0^T \exp(-H^{\mathrm{SD}}/k_B T)\,, \tag{1}$$

at least over several powers of ten. Here H^{SD} is the activation enthalpy of self-diffusion, which at atmospheric pressure is nearly identical to the activation energy E^{SD}, and D_0 is the preexponential factor. For the case of a defect mechanism we may write

$$D^T(T) = g f^T C^{\mathrm{eq}} D_{\mathrm{defect}}\,. \tag{2}$$

Here the geometrical factor g and the correlation factor f^T are numerical factors which are well known for various defect mechanisms. The concentration of defects in thermal equilibrium, C^{eq}, is given by

$$C^{\mathrm{eq}} = \exp(S^F/k_B T)\exp(-E^F/k_B T)\,, \tag{3}$$

where S^F is the formation entropy and E^F the formation energy of the defect (at atmospheric pressure we again do not distinguish between energy and enthalpy). Combining Eqs. (1)–(3), it becomes obvious that the diffusivity D_{defect} of the single defect is also given by an exponential temperature dependence, which is written as

$$D_{\mathrm{defect}} = D_{\mathrm{defect}}^0 \exp(-E^M/k_B T) \tag{4}$$

with the migration energy E^M and the preexponential factor D_{defect}^0, which are defined operationally via Eq. (4). Obviously, for a defect mechanism the activation energy E^{SD} is given by

$$E^{\mathrm{SD}} = E^F + E^M. \tag{5}$$

The objective of a theory of self-diffusion is to calculate the self-diffusion parameters E^{SD}, E^F, E^M, S^F, and D_{defect}^0 for various possible mechanisms and to check for consistency with experimental data.

For Li the formation energies E_I^F of various self-interstitial configurations as calculated [6] by the *ab initio* pseudopotential method are at least 40% larger than the experimentally obtained activation energy E^{SD}, so that the self-interstitial mechanism could be excluded as the dominant mechanism. The direct exchange mechanism could also be excluded because the *ab initio* pseudopotential calculations yielded [7] an activation energy which was a factor of about 2.5 larger than the experimental value. *Ab initio* calculations for extended ring mechanisms are lacking. In this Letter we represent *ab initio* calculations of the above discussed self-diffusion parameters for the monovacancy mechanism (index 1V) in Li. To our knowledge, these are the first parameter-free calculations of the absolute thermal monovacancy concentration and of the self-diffusion constant for monovacancies in a metal. It will be shown that our *ab initio* data agree well with the experimental self-diffusion data in Li at high temperatures.

The calculations were performed within the supercell formalism and in local-density approximation. A nonlocal, nonlinear [8], optimally smooth norm-conserving pseudopotential [9] was used. All results were tested for convergence with respect to the number of plane waves in the basis set and the number of k points used for the sampling of the Brillouin zone. In our *ab initio* calculations all quantities are evaluated for the fixed theoretical zero-temperature lattice constant of 6.34 a.u. for the ideal Li crystal (superscript flc), whereas experiments refer to the quantities for constant pressure appearing in Eqs. (1)–(5). Neglecting the explicit temperature dependence of $E_{1\mathrm{V}}^{F,\mathrm{flc}}$ due to the excitation of phonons (which according to our calculations is negligibly small) as well as the temperature dependence of $\beta_p \Omega_0 \partial E_{1\mathrm{V}}^{F,\mathrm{flc}}/\partial\Omega_0$ (β_p is the thermal volume expansion coefficient at constant pressure, Ω_0 is the atomic volume), and assuming $\partial S_{1\mathrm{V}}^{F,\mathrm{flc}}/\partial\Omega_0 = 0$ (this might be risky according to Harding [10]), the following relations hold at zero pressure [10,11]: $E_{1\mathrm{V}}^{F}(T) = E_{1\mathrm{V}}^{F,\mathrm{flc}}(T = 0)$ and $S_{1\mathrm{V}}^{F}(T) = S_{1\mathrm{V}}^{F,\mathrm{flc}}(T) + \beta_p \Delta V/\kappa_T$, where ΔV is the local relaxation volume of the vacancy and κ_T denotes the compressibility at constant T. For β_p we inserted the experimental value of 168×10^{-6}/K (obtained as an average value between 293 and 368 K), and for κ_T and ΔV we used or own *ab initio* results [6] for zero temperature. For the migration quantities, analogous equations hold with the relaxation volume replaced by the migration volume. Because the vacancy migration volume is generally assumed to be very small, we have $E_{1\mathrm{V}}^{M}(T) = E_{1\mathrm{V}}^{M,\mathrm{flc}}(0)$ and $S_{1\mathrm{V}}^{M}(T) \approx S_{1\mathrm{V}}^{M,\mathrm{flc}}(T)$. The approximate conversion from fixed lattice constant to fixed pressure has a big influence on the results, as shown in Figs. 2 and 3 below.

Vacancy concentration.—The vacancy formation energy was calculated along the lines described in Ref. [6] for a supercell containing 54 sites, yielding a value of $E_{1\mathrm{V}}^{F} = 0.54$ eV. Concerning the convergence with respect to the supercell size, it is generally assumed [12] that, for simple metals and reasonably large supercells, the part of the vacancy formation energy that depends on the supercell sizes originates almost exclusively from elastic interactions between the vacancies. We have corrected for these elastic interactions [13], arriving at a final value of $E_{1\mathrm{V}}^{F} = 0.52$ eV.

The formation entropy $S_{1\mathrm{V}}^{F}$ results from the modification of the vibrational entropy when a vacancy is introduced in the crystal. Within the supercell approach it is calculated according to

$$S_{1\mathrm{V}}^{F,\mathrm{flc}} = S(N-1,1) - \frac{N-1}{N} S(N,0)\,, \tag{6}$$

where $S(N-1,1)$ and $S(N,0)$ are the vibrational entropies for the supercell with $N - 1 = 53$ atoms (and one vacancy) and for the perfect supercell, respectively. In harmonic approximation the vibrational entropy thereby is given by

$$S = k_B \sum_i \left\{ \frac{\hbar\omega_i}{k_B T[\exp(\hbar\omega_i/k_B T) - 1]} - \ln[1 - \exp(-\hbar\omega_i/k_B T)] \right\}, \tag{7}$$

where the sum runs over all phonon states. The phonon states were calculated by the *ab initio* force-constant method along the lines described in Ref. [14]. Thereby the force-constant matrix is obtained from the *ab initio* forces exerted by single displaced atoms on all the other undisplaced atoms in the supercell. Although we used rather small displacements of 0.015 elementary lattice constant, the calculations yielded slight anharmonicities, which are corrected for along the lines given in Ref. [15]. Because of symmetry the displacement of the central atom of the supercell yields all elements of the force-constant matrix for a perfect bcc crystal [14]. In contrast, for a supercell containing a vacancy, 20 different calculations are required to obtain the full force-constant matrix, including the correction for anharmonicities. We determined the couplings up to the fifth nearest-neighbor couplings, which was sufficient to reproduce [14] very accurately [16] the experimentally observed phonon dispersion curves for the perfect crystal. An extensive discussion of the finite-size effects is given in Ref. [14]. From the force-constant matrix the dynamical matrix is determined by a Fourier transformation, and the phonon frequencies for arbitrary wave vectors are evaluated by a diagonalization of the matrix. For the calculation of $S_{1\mathrm{V}}^{F}$ in Si, a similar approach has been used by Biernacki *et al.* [17], whereas Blöchl *et al.* [5] applied the so-called local harmonic approximation, and Smargiassi and Madden [18] used for Na a thermodynamic integration method based on an *ab initio* molecular dynamics simulation.

Figure 1 shows the temperature dependence of $S_{1\mathrm{V}}^{F,\mathrm{flc}}$ together with the results obtained from a very simple model (dashed line), where we describe the introduction of the vacancy just by cutting the couplings between the removed atom and all other atoms while keeping the couplings among the remaining atoms unchanged. In reality, these latter couplings will be modified due to the change of the electronic structure induced by the vacancy. It becomes clear from Fig. 1 that this simple model does not suffice. The formation entropy increases strongly with increasing temperature at low T but varies only slightly with temperature for $T > 200$ K.

The absolute concentrations of vacancies in thermal equilibrium as calculated from Eq. (3) are shown in Fig. 2. They are considerably smaller than those given by the $\Delta l/l - \Delta a/a$ experiment of Feder and Charbnau [19]. This experiment yielded a very low formation energy of $E_{1\mathrm{V}}^{F} = 0.34$ eV, which is in strong disagreement with all available theoretical predictions [6]. It is highly imperative to repeat this very difficult experiment.

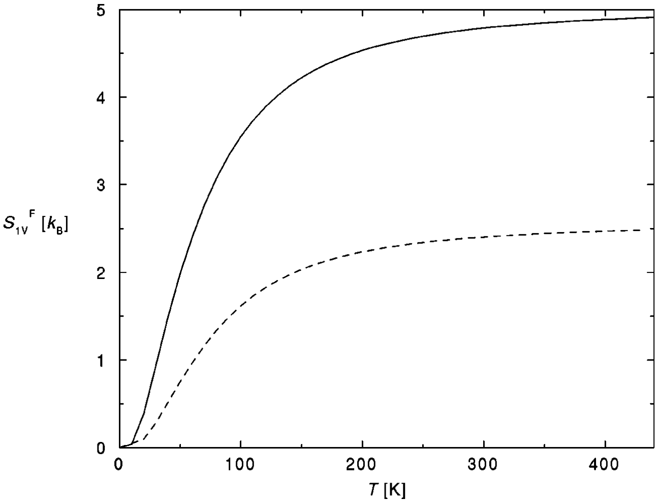

FIG. 1. Temperature dependence of the vacancy formation entropy at fixed lattice constant for Li (solid line). For the meaning of the dashed line, see text.

Diffusivity.—The diffusivity D_{defect} may, in principle, be calculated by an *ab initio* molecular dynamics study, as it was done for the vacancy in Si by Blöchl *et al.* [5]. To achieve reasonable statistical accuracy, this method requires an enormous computational effort. We determined D_{defect} within the framework of the transition-state theory (TST) [20]. In this theory, the migration energy $E_{1\mathrm{V}}^{M}$ is given by the energy difference between two static, fully relaxed configurations, the saddle-point configuration with the moving atom halfway in the $\langle 111 \rangle$ direction to the vacant lattice site and the initial configuration before the jump of the atom. We obtained a value of $E_{1\mathrm{V}}^{M} = 0.055$ eV (yielding $E^{\mathrm{SD}} = 0.575$ eV). Usually it is assumed [1] that the TST theory is strictly valid only if $E_{1\mathrm{V}}^{M}$ is larger than at least $3k_BT$. Because this is not fulfilled in the present case, we have tested [21] the TST for Na (which exhibits, according to our calculations, about the same value of $E_{1\mathrm{V}}^{M}$) by an *ab initio* molecular dynamics study based on the semiempirical potentials of Rasolt and Taylor [22]. It turned out that the migration energy obtained dynamically via the mean-square displacement of the vacancy agreed very well with the value according to the TST. For D_{defect}^{0} the TST yields for nearest-neighbor jumps of a vacancy in a cubic crystal

$$D_{\mathrm{defect}}^{0} = \nu_0 a^2 \exp(S_{1\mathrm{V}}^{M}/k_B)\,, \tag{8}$$

where a is the lattice constant, ν_0 the attempt frequency, and $S_{1\mathrm{V}}^{M}$ the migration entropy which is related to the harmonic vibrations around the saddle-point configuration. Because $S_{1\mathrm{V}}^{M}$ is generally assumed to be much smaller than $S_{1\mathrm{V}}^{F}$, we insert $S_{1\mathrm{V}}^{M} = 0k_B$. For the attempt frequency we use Flynn's [23] value of $\nu_0 = \sqrt{3/5}\,\nu_{\mathrm{Debye}} = 6.8$ THz.

The values for $D^T(T)$ at high temperatures as obtained from Eq. (2) are shown in Fig. 3, together with experimental data from mass spectroscopy [24] and from pulsed field-gradient NMR experiments [25]. The experimental data are between the theoretical results obtained for fixed zero-temperature lattice constant and for fixed pressure. It should be noted that the slopes of the theoretical and experimental curve [25] agree almost perfectly. We think that the agreement is also astonishingly good for the absolute values, especially in view of the uncertainties involved in the conversion between fixed lattice

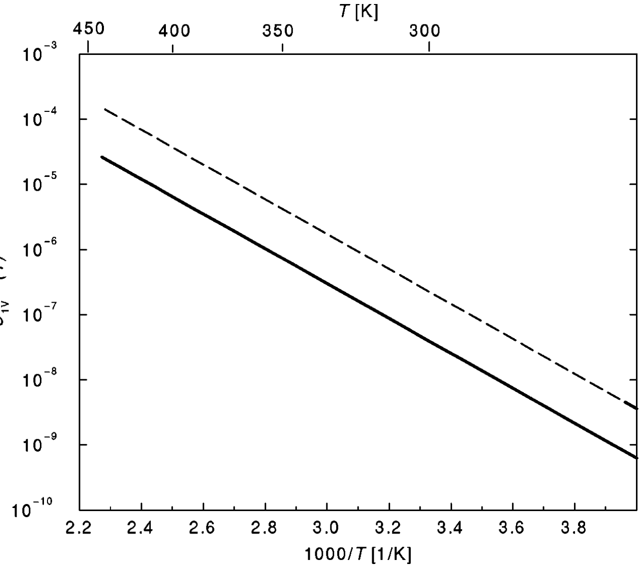

FIG. 2. Temperature dependence of the concentration of thermal monovacancies in Li. Full line (dashed line) for fixed pressure (fixed lattice constant).

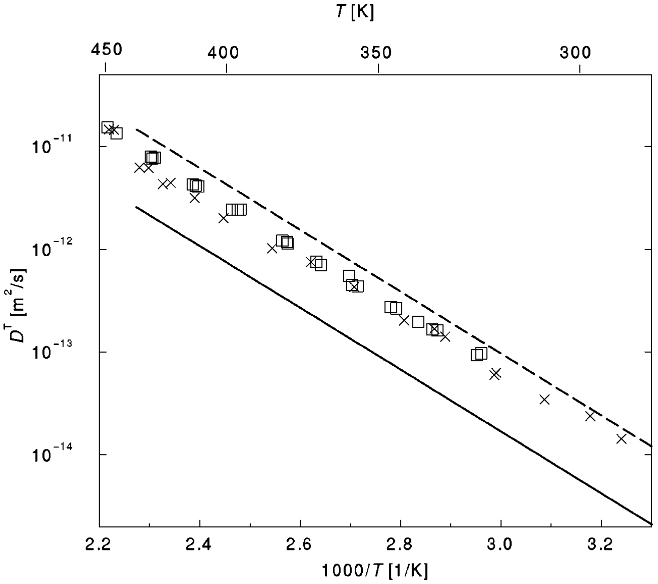

FIG. 3. Temperature dependence of the tracer self-diffusion constant in Li; (□) pulsed field-gradient NMR [25], (×) mass spectroscopy [24]. Full line (dashed line) for fixed pressure (fixed lattice constant).

constant and fixed pressure. Altogether, this demonstrates that the experimental data for the tracer self-diffusion in Li at high temperatures [26] are compatible with the notion of a monovacancy mechanism.

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