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Theory of self-diffusion in alkali metals: II. The influence of divacancies in Li

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Abstract. The formation energies and the binding energies of divacancies in bcc Li are calculated using the *ab initio* electron theory in a supercell approach. The results show that the activation energy for self-diffusion via divacancies should be much larger than that for self-diffusion via monovacancies. This is in contrast to the case for an analysis of the experimental self-diffusion data from the nuclear magnetic resonance relaxation rates in terms of a combined monovacancy–divacancy mechanism which would yield similar activation energies for monovacancies and divacancies. It is therefore concluded that a contribution from divacancies cannot explain the observed curvature of the Arrhenius plot for the self-diffusion data for Li at high temperatures.

1. Introduction

In the preceding paper [1], hereafter denoted as part I, the contribution of monovacancies to the self-diffusion coefficient in bcc Li, Na, and K has been calculated. The present paper considers the contribution of divacancies. The interest in divacancies is motivated by the fact that the Arrhenius plots for the self-diffusion coefficient in bcc Li [2], Na [3,4], and K [5] are curved at high temperatures. This curvature may be interpreted in two ways:

- (a) by a temperature dependence of the activation energy;
- (b) by contributions from more than one self-diffusion mechanism, e.g., with activation energies E_{1V}^{SD} and E_{2V}^{SD} for monovacancies and divacancies [6].

By analysing within the framework of the monovacancy–divacancy mechanism [6] the NMR spin–lattice relaxation rates obtained by the field-cycling method, Feinauer [2] obtained for the parameter

$$E_{21} = \frac{E_{2V}^{SD} - E_{1V}^{SD}}{E_{1V}^{SD}} \quad (1)$$

a very small value of $E_{21} = 0.05 \pm 0.02$ for the self-diffusion of ${}^6\text{Li}$. Taking into account that the formation energies of monovacancies in alkali metals are much larger than the migration energies (table 2 of part I), this small value would imply that in Li the formation energy of divacancies is only slightly larger than the formation energy of monovacancies, i.e., that the (modulus of the) binding energy of the two vacancies forming the divacancy is of the same size as the monovacancy formation energy. For Na, Mundy [3] performed an analysis of the

curved Arrhenius plot for the data from radiotracer experiments by means of a superposition of two exponentials with two activation energies. If these two activation energies are assigned to monovacancies and divacancies, one obtains $E_{21} = 0.348$ which is more reasonable but still small. Neumann *et al* [4] performed radiotracer experiments for Na in a temperature range which included rather low temperatures. They analysed their Arrhenius plot by means of three exponentials, assigning the smallest activation energy to an enhanced self-diffusion related to the low-temperature martensitic transformation. Interpreting the two higher activation energies in terms of monovacancies and divacancies yields $E_{21} = 0.512$. For K [5], a two-exponential fit for the Arrhenius plot would yield $E_{21} = 0.262$.

In the present part of the paper, part II, we calculate by the *ab initio* Kohn–Sham (KS) method and by calculations within the framework of the orbital-free density functional theory (OF-DFT) described in part I the formation energies and the binding energies of various divacancy configurations in bcc Li. The binding energy E^b is defined as

$$E^b = E_{2V}^f - 2 E_{1V}^f \quad (2)$$

where E_{2V}^f and E_{1V}^f are the formation energies of divacancies and monovacancies, and for bound divacancies we have $E^b < 0$.

2. Computational method and results

The quantities E_{2V}^f and E^b depend on the relative positions of the two monovacancies which form the divacancy, and we have determined these quantities for the case where the second monovacancy is in the k th-nearest-neighbour shell of the first monovacancy, with k up to 5. The calculations were performed by the supercell method [7], i.e., large supercells containing N sites and a monovacancy or a divacancy were repeated periodically. The structural relaxation of the atoms around the vacancies and the volume relaxation of the supercell due to the introduction of the vacancies were taken into account. The formation energies are given by

$$E_{1V}^f = E(N - 1, 1, V') - E(N, 0, V) + \frac{1}{N} E(N, 0, V) \quad (3)$$

$$E_{2V}^f = E(N - 2, 2, V'') - E(N, 0, V) + \frac{2}{N} E(N, 0, V). \quad (4)$$

Here $E(N - 1, 1, V')$ is the energy of the supercell with $N - 1$ atoms and one monovacancy at volume V' , $E(N - 2, 2, V'')$ is the energy of the supercell with $N - 2$ atoms and one divacancy at volume V'' , and $E(N, 0, V)$ is the energy of the perfect supercell with N atoms, no defect, and at equilibrium volume V . Neglecting the volume relaxation means that we insert $V' = V'' = V$. In calculations including volume relaxation we insert for V' or V'' the respective volumes obtained by minimizing $E(N - 1, 1, V')$ or $E(N - 2, 2, V'')$ with respect to the volume of the supercell while fixing the cubic shape of the supercell. The divacancy formation volume is given by $\Omega_{2V}^f = V'' - V + 2\Omega_0$, where Ω_0 is the atomic volume. In principle, one should allow an anisotropic change of the supercell shape when introducing the divacancy. Our test calculations for the case of a divacancy with $k = 2$ formed by monovacancies in the next-nearest-neighbour distance showed that the effect of this anisotropic distortion of the supercell on the divacancy formation energy is probably rather small, and because of the very large numerical effort we therefore considered isotropic volume relaxations only.

The convergence of the results with respect to the supercell size may be critical. In the supercell containing 54 sites used for the KS calculations, the distance between the monovacancies forming a divacancy with $k = 4$ is equal to the distance of a monovacancy to another monovacancy in the periodically repeated supercell. In this case we divided the binding energy

so obtained by a factor of 2 because there are altogether two divacancy bonds per supercell. The divacancy with $k = 5$ was even unstable in this supercell: the two monovacancies are arranged in a $\langle 111 \rangle$ direction, and due to the structural relaxation the remaining four atoms which are located along $\langle 111 \rangle$ in this supercell are arranged with equal separation along this line, so the final configuration can no longer be called a divacancy. To test for finite-size effects we therefore performed calculations with the OF-DFT both for a supercell with 54 sites and for one with 128 sites. In part I of the paper it has been shown that for Li the strengths of the couplings between the atoms as obtained by the OF-DFT decay more rapidly than those obtained by the KS calculation. Therefore, the calculations with the OF-DFT do not represent a strict test of the finite-size effects for the KS calculations but should give at least a rough estimate of the finite-size effect. It turned out that the results for the formation and binding energies of divacancies obtained from the OD-DFT for configurations with $k = 1$ to $k = 4$ depend only slightly on the supercell size and we therefore hope that the KS calculations for the supercell with 54 atoms are also reasonably well converged.

Tables 1 and 2 represent our results for the supercell with 54 atoms, obtained by the KS formalism and by the OF-DFT. (The small discrepancy between the monovacancy formation energy of 0.546 eV in table 1 and the value of 0.53 eV given in table 2 of part I results from the fact that in the latter case we have corrected for the residual elastic finite-size effect according to equation (21) of part I.) It is obvious that both the structural relaxation and the volume relaxation have to be taken into account in order to obtain reliable values for the binding energy E^b . Sometimes the binding energy even has the wrong sign when neglecting the

Table 1. The formation energies E_{2V}^f for divacancies in Li (in eV) with the two vacancies arranged on the k th-nearest-neighbour shells, with $k = 1, 2, 3, 4$, the corresponding binding energies E^b (in meV), and the formation volumes (in atomic volumes Ω_0). The last column represents the values for the monovacancy. The symbols ur, sr, and sr + vr denote calculations without any relaxation, with structural relaxation, and with combined structural and isotropic volume relaxation, respectively. The calculation is performed by the KS formalism for supercells with 54 sites.

k		1	2	3	4	1V
E^f	ur	1.234	1.199	1.321	1.316	0.651
	sr	1.076	0.941	1.131	1.041	0.548
	sr + vr	1.061	0.915	1.117	1.021	0.546
E^b	ur	-67.0	-102.6	19.9	7.5	—
	sr	-20.9	-155.8	34.5	-27.9	—
	sr + vr	-30.4	-176.7	25.1	-35.2	—
Ω^f		1.06	0.75	1.06	0.89	0.53

Table 2. As table 1, but now with OF-DFT calculations.

k		1	2	3	4	1V
E^f	ur	0.791	0.776	0.820	0.815	0.407
	sr	0.697	0.608	0.673	0.630	0.332
	sr + vr	0.686	0.588	0.658	0.613	0.329
E^b	ur	-22.6	-37.1	6.5	1.2	—
	sr	32.5	-56.7	8.3	-17.1	—
	sr + vr	28.7	-69.0	0.4	-22.3	—
Ω^f		1.15	0.89	1.00	0.95	0.54

relaxation effects. The OF-DFT theory yields smaller absolute values for the binding energies than the more accurate KS calculations, and for the configuration with $k = 1$ there is even another sign. In both calculations the binding is strongest for the configuration with $k = 2$. The formation volume of the divacancy is about one atomic volume in both calculations, and it is smallest for the configuration with $k = 2$.

3. Discussion and conclusions

In the following we consider the quantity

$$\tilde{E}_{21} = \frac{E_{2V}^f - E_{1V}^{SD}}{E_{1V}^{SD}} \quad (5)$$

which represents a lower limit for E_{21} because the migration energy for divacancies is positive, i.e., $E_{2V}^{SD} > E_{2V}^f$. Inserting our results from the KS calculations (for E^{SD} see table 2 of part I), we obtain the numbers given in table 3. These numbers are much larger than the value of $E_{21} = 0.05 \pm 0.02$ which is obtained when the NMR spin–lattice relaxation rates are analysed in terms of the monovacancy–divacancy mechanism. We cannot imagine that this discrepancy would become considerably smaller if KS calculations for larger supercells were performed. We therefore conclude that in bcc Li the contribution of divacancies to the self-diffusion cannot explain the curvature of the Arrhenius plot for the diffusion data.

Table 3. The values of \tilde{E}_{21} calculated by the KS formalism for bcc Li.

k	1	2	3	4
\tilde{E}_{21}	0.77	0.52	0.86	0.70

References

- [1] Schott V, Fähnle M and Madden P A 2000 *J. Phys.: Condens. Matter* **12** 1173
- [2] Feinauer A 1993 *PhD Thesis* University of Stuttgart
- [3] Mundy J N 1971 *Phys. Rev. B* **3** 2431
- [4] Neumann M, Scharwaechter P, Seeger A, Frank W, Freitag K, Konuma M and Majer G 1997 *Defect Diffusion Forum* **143–147** 85
- [5] Mundy J N, Miller T E and Porte R J 1971 *Phys. Rev. B* **3** 2445
- [6] Seeger A and Mehrer H 1970 *Vacancies and Interstitials in Metals* ed A Seeger, D Schumacher, W Schilling and J Diehl (Amsterdam: North-Holland) p 1
- [7] Breier U, Frank W, Elsässer C, Fähnle M and Seeger A 1994 *Phys. Rev. B* **50** 5928