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LETTER TO THE EDITOR

First-principles calculation of the relaxation around a vacancy and the vacancy formation energy in BCC Li

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Abstract. The formation energy and the formation volume of a vacancy in BCC Li are calculated by means of *ab initio* total energy calculations. The structural relaxation of the atoms surrounding the vacancy was determined using the Hellman-Feynman forces.

Whereas it is usually assumed that in metals self-diffusion is determined by vacancy mechanisms, there are hints from nuclear magnetic resonance experiments (Messer *et al* 1989) that in solid Li self-interstitials might play a role at high temperatures. We therefore started a programme to investigate both experimentally and theoretically the electric field gradients at a regular Li site next to a vacancy and next to a Li interstitial. In this letter we report on the first step in this direction, i.e. the calculation of the vacancy formation energy, the formation volume and the structural relaxation near the vacancy using first principles techniques.

Due to the complexity of the problem, these quantities could in the past only be calculated with empirical pair potential models (Ho 1971, Das *et al* 1975, Jacucci and Taylor 1979). Increased computer power and advances in computational techniques make it now possible to perform *ab initio* calculations for defect structures. Our calculations reported below are done within the local density functional formalism (Kohn and Sham 1965). The only essential approximation is the use of a local exchange-correlation functional, which we took to be of the Hedin-Lundqvist (1971) form. Norm conserving pseudopotentials are used (Hamann *et al* 1979), which reproduce the scattering power of the full atom potential for the valence electrons correctly, and the Bloch wavefunctions are expanded in a plane-wave basis set. The plane-wave pseudopotential method is ideally suited for structural properties of 'simple' metals, and has been successfully applied to determine the vacancy formation energy of Al (see, e.g., Gillan 1989, Finnis 1990). We note that similar work in this direction is being performed by Benedek *et al* (1990).

The pseudopotential was constructed according to Hamann *et al* (1979), with a reference configuration of $2s^{0.5}2p^{0.4}3d^{0.1}$ and cut-off radii $r_{c,s} = r_{c,p} = r_{c,d} = 1.2$ au. The partial-core correction (Louie *et al* 1982) was implemented as suggested by Dacarogna and Cohen (1986). The transferability of the pseudopotential was tested for several excited states of the Li atom by comparing excitation energies and eigenvalues computed

with the pseudopotential and all electron calculations. For the configurations we have tested, excitation energies computed with pseudopotentials are within 10^{-4} Ryd of the all electron results, whereas the eigenvalues are within 10^{-6} Ryd. Following this, a bulk calculation was performed using the momentum-space formalism of Ihm *et al* (1979). The partial-core correction is essential to get reasonable values for the lattice constant (see table 1). For the perfect crystal, the convergence behaviour (dependence of the total energy on the energy cut-off and the number of k -points) was examined carefully.

Table 1. Results of bulk calculations and influence of the partial-core correction.

	Partial-core correction		Experiment ^a
	With	Without	
Lattice constant (Å)	3.534	3.269	3.491
Bulk modulus (10^{11} N mm ⁻²)	0.133	0.148	0.116
Binding energy (eV)	-1.48	-1.70	-1.63

^aKittel (1983).

The vacancy formation energy was then calculated by a supercell method similar to that of Gillan (1989)

$$E_v^F = E(N-1, 1, V') - \frac{N-1}{N} E(N, 0, N\Omega_0) \quad (1)$$

where $E(N, n, V)$ denotes the total energy of a supercell with N atoms, n vacancies and a volume V . Ω_0 is the volume of one atom in the perfect lattice, V' is the relaxed volume of the supercell with a vacancy. Obviously, the calculation of E_v^F requires only two supercell calculations with periodic boundary conditions. Nevertheless, equation (1) implicitly accounts (Braun 1990) for the fact that in the real process of vacancy formation the atom removed from the regular lattice site is inserted at a 'typical' surface site ('Halbkristall-Lage'), thereby regaining binding energy.

The vacancy formation volume can be defined via the change of the macroscopic dimensions upon formation of vacancies, where for a precise definition the geometry of the sample must be specified:

(i) For an infinitely extended sample without surface it is given by $(\Delta V^\infty + \Omega_0)$, where ΔV^∞ is the relaxation volume for the infinite system.

(ii) For a macroscopic sample with free surface it is denoted as $V_{lv}^F = (\Delta V + \Omega_0)$, where ΔV is the relaxation volume for the finite system.

(iii) For a supercell geometry which is different from (i) and (ii) it is defined by the quantity

$$\Omega^F = V' - (N-1)\Omega_0. \quad (2)$$

Alternatively, the vacancy formation volume can be derived thermodynamically from the pressure derivative of the free enthalpy of vacancy formation, which may be written (Jacucci and Taylor 1979) as

$$\Omega_{th}^F = -\Omega_0 K_T \Delta P_v \quad (3)$$

where ΔP_V is the pressure increase upon formation of the defect at constant volume and K_T the compressibility.

The value of N in equation (1) should be large enough to minimize the interaction between vacancies in different supercells. We examined the cases $N = 16$ and $N = 54$, which lead to a simple cubic supercell geometry with superlattice constants of $2a_0$ and $3a_0$, respectively, where a_0 is the lattice constant of the simple lattice. The plane-wave basis set was restricted by a maximum energy cut-off $E_c = 10.5$ Ryd, and the number n of k -points in the irreducible Brillouin zone (IBZ) was limited to 10 in the case of $N = 16$ and 20 for $N = 54$. Note that this corresponds to a number n_1 of 112 and 728 k -points, respectively, in the IBZ of a one-atom unit cell. To improve the k -point convergence, we used the Gaussian smearing method (Fu and Ho 1983, Ho *et al* 1983) with a Gaussian smearing of 0.2 eV to determine the weights of the k -points. Because the calculations are very time consuming, we then have performed the relaxations for the 54-atom supercell only for a maximum of $n = 4$ ($n_1 = 30$). For the thus determined positions of the atoms at $E_c = 10.5$ Ryd we have then increased the number of n and n_1 when calculating the formation energy.

The relaxation was performed iteratively. First a structural relaxation was made with a fixed lattice constant, where the atoms were moved according to the Hellman-Feynman forces, calculated as described by Ihm *et al* (1979), with an additional term to take into account the partial-core correction ($\sum_G \delta\rho^{\text{core}}(\mathbf{G})\mu_{xc}(\mathbf{G})$ which has to be added to δE_{tot}). The relaxation was continued until the forces were zero and an energy minimum was reached. To minimize the computational effort, it was assumed that the relaxation would not break the symmetry of the system, which is reasonable for metals where predominantly central forces appear (Frank 1990). In the next step, a volume relaxation was performed, thereby fixing the relative positions of the atoms. This had to be done very carefully, as the vacancy formation volume is a very sensitive quantity. To get the best cancellation of errors, the vacancy formation energy $E_v^F(V')$ determined by supercell calculations at a volume V' was added to the energy of the ideal crystal at the same volume as was calculated using a one-atom cell with a higher cut-off $E_c = 16.5$ Ryd, 506 k -points in the IBZ and fitted to a 'universal binding curve' (Rose *et al* 1981). This procedure yields an accurate expression for the energy of the system with a vacancy as a function of the volume and allows us to determine the equilibrium volume in a proper way. After that, a structural relaxation was performed again, but it turned out to be small so we could terminate the iteration at that point.

Figure 1 shows the results for the relaxation of the neighbouring atoms (without consideration of the volume relaxation). It should be noted that the finite size of the supercell suppresses the displacement u of the exterior atoms, as for $R = 2.6$ au. u has to be zero for geometrical reasons.

The results for the vacancy formation energy and volume are presented in table 2. Convergence with respect to basis size and k -point sampling can be deduced by comparing results obtained using different cut-off energies and k -point sets. It should be noted that the energy gain due to relaxation for $n = 4$ ($n_1 = 30$) is of the same order as the change of the formation energy when going to $n = 20$ ($n_1 = 728$). We believe that a small additional change of the atomic positions which would result if we performed the relaxations also at these higher values of n and n_1 does not modify the formation energy appreciably. It is gratifying that the geometrically and the thermodynamically calculated formation volumes agree well. We should be careful when we compare the theoretical results for the formation volumes with the experimentally determined quantities because the calculation pertains to an ordered array of

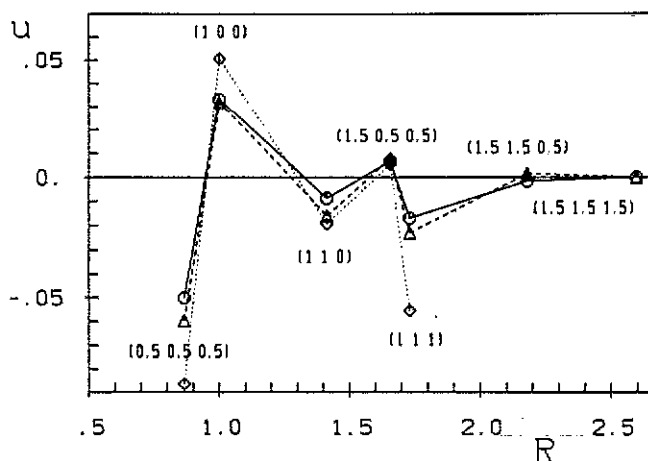


Figure 1. Relaxation of the neighbouring atoms around the vacancy. The displacement u is shown as a function of the distance R from the vacancy (all in lattice units). The full curves show our final result with $E_c = 10.5$ Ryd and four k -points, the broken curves show the result for $E_c = 8.5$ Ryd and one k -point. The dotted curves correspond to the result of Das *et al* (1975).

Table 2. Results for the vacancy formation energy E_v^F (in eV) and the formation volume (in units of Ω_0 , see text) for different values of N (number of atoms in the supercell), E_c (cut-off energy for the plane-wave basis) in Ryd and the number of k -points n and n_1 (see text).

N	E_c	k -points		E_v^F		Formation volume
		n	n_1	Without relaxation	With relaxation	
16	8.5	4	14	0.74	—	—
	8.5	10	112	0.54	—	—
54	8.5	1	8	0.77	0.59	$\Omega^F = 0.58, \Omega_{th}^F = 0.57$
	8.5	4 ^a	30	0.60	0.52	—
	10.5	4	30	—	0.53	$\Omega^F = 0.52, \Omega_{th}^F = 0.51$
	8.5	4 ^b	112	—	0.47	—
	10.5	4	112	—	0.47	—
	8.5	20	728	—	0.47	—
Ho ^c	(with local potential)		—	0.37	$\Omega^F = 0.53$	
	(with non-local potential)		—	0.46	$\Omega^F = 0.59$	
Jacucci and Taylor ^d			0.52	—	$\Omega_{th}^F = 0.43$	
Experiment			—	0.34 ± 0.04^e	$V_{1v}^F = 0.2-0.25^f$	

^ahigh symmetry k -points.

^blow symmetry k -points.

^cHo (1971).

^dJacucci and Taylor (1979).

^eFeder (1970).

^fSeeger (1973).

vacancies at a higher density than experimental situations (see the different definitions for Ω^F and V_{1V}^F above). It should be noted that our *ab initio* results for the vacancy formation volume as well as for the formation energy are very close to other *ab initio* results (Benedek 1990) and rather close to those obtained by empirical pair potential calculations.

We are now planning to consider interstitials in the same way and to examine the electric field gradients that occur on the neighbouring site.

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