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Ab initio calculation of the formation energy and the formation volume of monovacancies in Mo

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By means of the *ab initio* mixed-basis pseudopotential theory and the local-density approximation the formation energy E_{1V}^F and the formation volume V_{1V}^F of monovacancies in Mo are calculated with high accuracy—including the structural relaxation of the atoms around the vacancy—in order to explore the reliability of the *ab initio* electron theory for the treatment of vacancies in transition metals. The calculated formation energy $E_{1V}^F=(2.9\pm0.1)$ eV is in excellent agreement with experimental data from positron annihilation. For the formation volume a value of (0.6 ± 0.1) atomic volume is obtained. [S0163-1829(97)00945-4]

One of the objectives of materials science is to combine phenomenological theories (statistical mechanics, continuum theories) with microscopic theories in order to understand the mesoscopic and macroscopic behavior of materials from the viewpoint of the electronic structure. An example is the theory of self-diffusion via atomic defects. In this case the macroscopic material parameter, i.e., the diffusion constant D, may be directly related to microscopic parameters like the energies, entropies, and volumes of defect formation and defect migration via equilibrium statistical mechanics (for the formation) and via the transition-state theory[1] (for the migration). The contribution of the microscopic theory is to calculate these microscopic parameters and to explain the differences between various systems on the basis of their structure and electronic properties. To obtain highly accurate and reliable results it is thereby important to perform the microscopic calculations from first principles (*ab initio*), i.e., without the use of adjustable parameters. The capability of such calculations has been most convincingly demonstrated for silicon[2] and for the simple metals Li,[3] Na,[4] and Al.[5] For instance, for Na and Al where highly accurate experimental data exist, there is an excellent agreement between theory and experiment for the formation energy E_{1V}^F of monovacancies. For Li reliable data for E_{1V}^F are missing, but there are accurate results for the activation energy for self-diffusion which at high temperatures agree very well with the theoretical result[3] for the activation energy of monovacancies. In all calculations it turned out that it is absolutely necessary to refrain from approximations for the crystal potential,[6–8] i.e., to perform a full-potential calculation, and to take into account the structural relaxation of the atoms near the atomic defects.

In recent years calculations on this level have been performed for intermetallic compounds of transition metals and main group elements, for instance, NiAl,[9] FeAl,[9–11] Fe_3Al,[11,12] and Ni_3Al.[13] In these systems the properties of the electronic structure are very complicated and the use of *ab initio* methods is therefore indeed absolutely indispensable. The comparison with experimental data is more complicated than in elementary metals because (i) there is a coexistence of various types of defects, (ii) the microscopic parameters depend on the composition which is sometimes hard to control with high accuracy in the experiment, and (iii) the sample homogeneity is not always guaranteed. In view of these problems it is desirable to test the reliability of the *ab initio* calculations first for elementary transition metals. Curiously enough, there are so far no *ab initio* full-potential calculations for vacancies in transition metals which are on the same level as those for elementary metals: In the full-potential Korringa-Kohn-Rostoker (KKR)-Green's-function calculations[7] for fcc and hcp transition metals, in the full-potential linear-muffin-tin-orbital (FLMTO) calculations[14] for Cu, Ag, and Rh and in the FLMTO calculations[15] for bcc V, Cr, Nb, Mo, Ta, W, and fcc Ni, Cu, Pd, Ag, Pt, Au the structural relaxation of the atoms around the vacancy was neglected. (Most recently,[16] the lattice distortion around a vacancy in Cu has been included in the KKR-Green's-function calculation, and the tools to study relaxations around vacancies in bcc metals based on this method have been implemented.) In the present paper we report on *ab initio* calculations for the vacancy formation energy and the vacancy formation volume in Mo on a maximum possible, while still feasible, level of accuracy, including structural relaxations, with two objectives. First, we want to demonstrate that *ab initio* calculations with the local-density approximation[17] are a powerful tool to determine vacancy formation energies not only in simple metals but also in transition metals. Second, we want to demonstrate that defect calculations for transition metals can be performed with the *ab initio* pseudopotential method, if the basis set of plane waves is augmented by a few localized orbitals. Although such mixed-basis pseudopotential calculations[18] have been successfully performed for transition metals for nearly two decades, it is still often stated[7,15] that pseudopotential methods are difficult to apply for transition metals. The big advantage of the mixed-basis pseudopotential method is that the forces on atoms may be calculated simply and accurately (as becomes obvious from an extensive comparison of the forces calculated directly or via the energy change upon displacement), so that the investigation of the structural relaxation is feasible.

The calculations were performed with the local-density approximation[17] (LDA) and the exchange-correlation functional of Ref. 19. The *ab initio* mixed-basis pseudopotential method[18] with a basis set consisting of plane waves (energy cutoff E_c) and five nonoverlapping d orbitals per atom was used, for which recently an extended computer code with improved accuracy (especially for the forces) and efficiency has been developed.[20] The d orbitals are constructed from an atomic pseudowave function by smoothly cutting off the tail beyond a certain cutoff radius. This cutoff is done by multiplying the radial part of the wave function with 1 minus a Gaussian function centered at the cutoff radius and varying the Gaussian width parameter to minimize the energy of the bcc ground state. The optimally smooth *ab initio* pseudopotentials of Vanderbilt[21] with a reference configuration $[\mathrm{Kr}]4d^{4.5}5s^{0.7}5p^{0.8}$ and $r_{c,s}=1.87$ a.u., $r_{c,p}=2.12$ a.u., and $r_{c,d}=1.16$ a.u. were applied. The cutoff radius r_{pc} for the partial-core correction[22] was chosen in such a way (0.94 a.u.) that the outermost maximum of the core-charge density appeared for $r>r_{\mathrm{pc}}$. The $4p$ states were treated as true core states (for the problem of $4p$ states in Mo see, for instance, Ref. 23). The transferability of the pseudopotential was tested for several excited atomic states. The excitation energies computed with the pseudopotential agreed with the all-electron results within about 1 mRy.

The cubic lattice parameter a_0 and the bulk modulus K of the perfect lattice as obtained by converging the results with respect to the plane-wave cutoff E_c (up to 24 Ry) and the number of k points used for the sampling of the Brillouin zone (up to 240) are $a_0=3.135$ Å and $K=2.77$ Mbar, which compares rather well (see, for instance, Table I of Ref. 15) with other theoretical and experimental ($a_0=3.15$ Å, $K=2.73$ Mbar) values. It should be noted that the results are well converged already for $E_c=12.5$ Ry and for 56 k points in the irreducible part of the Brillouin zone).

For the computations of the vacancy properties periodic arrangements of supercells with $N=8$, 16, 27, 32, and 54 atoms in the defect-free cells, respectively, were used. The vacancies were inserted at the supercell centers so that periodic arrangements of vacancies with bcc (8,27), sc (16, 54), and fcc (32) symmetry arise. The formation energies were calculated according to

$$E_{1V}^{F}=E(N-1,1,\Omega_{1V})-\frac{N-1}{N}\,E(N,0,\Omega). \qquad (1)$$

Here $E(N-1,1,\Omega_{1V})$ denotes the energy of a supercell with $N-1$ atoms and one vacancy at the volume Ω_{1V} of the supercell, and $E(N,0,\Omega)$ is the energy of an ideal supercell with N atoms at the volume Ω. In order to obtain a maximum possible error cancellation, we evaluated both terms in Eq. (1) for the same E_c and the same number of k points. The relaxation of the atomic positions around the vacancy was performed by first moving the atoms until the calculated forces on the atoms are nearly zero (''structural relaxation''). During this first step the supercell volume was kept constant, and we inserted for Ω_{1V} and Ω the experimental equilibrium volume. In a second step both the ideal supercell and the supercell with vacancy were allowed to expand or shrink homogeneously (''volume relaxation'') until the total energies reached their respective minimum at the volumes $N\Omega_0$ and $\Omega_{1V,0}$. The volume difference, $\Delta V_{1V}^{F}=\Omega_{1V,0}-N\Omega_0$ thereby corresponds to the relaxation volume of the vacancy, i.e., to the change of the volume of a finite crystal with traction-free surfaces upon removal of an atom, and $V_{1V}^{F}=\Delta V_{1V}^{F}+\Omega_0$ is the vacancy formation volume (see, for instance, Ref. 4). In a third step we checked whether forces on the atoms reappeared after the volume relaxation which would give rise to a noticeable structural relaxation, but this was not the case. The combined effect of structural and volume relaxation is denoted as ''total relaxation'' in the following.

As outlined, for instance, in Refs. 4, 8, 10, the results for E_{1V}^{F} and V_{1V}^{F} have to be tested for convergence with respect to the energy cutoff E_c, the number of k points used for the Brillouin-zone sampling and the number N of atoms in the ideal supercell. Concerning the convergence with respect to N it turned out[4,8] that for systems with simple electronic structure that part of E_{1V}^{F} which depends on the supercell size N originates almost exclusively from elastic interactions between the periodically arranged vacancies, whereas the electronic interaction is screened almost perfectly even for small N. For Na, for instance, the energy of the residual elastic interactions for $N=54$ amounts[4] to 0.01–0.02 eV only. In contrast, for FeAl the electronic interaction is much stronger,[10] probably because the Fermi energy is located at the right-hand slope of a sharp peak in the electronic density of states, and therefore E_{1V}^{F} depends very sensitively on N. In ideal Mo the Fermi energy falls in a pronounced valley of the electronic density of states, and we therefore expect a fast convergence of E_{1V}^{F} with respect to N. In order to facilitate the comparison of the convergence with respect to the number of k points for the supercell sizes, we exhibit in Table I the number n_1 of k points which had to be used in a one-atom supercell to get the same single-particle states as in a perfect N-atom supercell, i.e., we used ''equivalent'' sets of

TABLE I. Results for E_{1V}^F (in eV) for different N, n_1, E_c, and various degrees of structural relaxation.

N	8 (bcc)		16 (sc)		27 (bcc)		32 (fcc)		54 (sc)	
E_c (Ry)	12.5	16.0	12.5	16.0	12.5	16.0	12.5	16.0	12.5	16.0
n_1										
20										
No relaxation		3.74			2.70				2.94	
Structural relaxation									2.86	
Total relaxation										
40										
No relaxation	3.72	3.72	3.34	3.33			3.12			
Structural relaxation			3.32							
Total relaxation			3.07							
112										
No relaxation		3.72	3.28	3.27	3.02	3.02	3.13		3.16	
Structural relaxation			3.27		2.98				3.09	
Total relaxation			3.00						2.90	
240										
No relaxation		3.75	3.33				3.14			
Structural relaxation			3.31							
Total relaxation										
330										
No relaxation		3.74			3.02				3.07	
Structural relaxation					2.98					
Total relaxation										

k points. The special k-point sets of Chadi and Cohen[24] and a Gaussian broadening scheme[25] with a smearing parameter of 0.1 eV was applied. For a 16-atom supercell we used in addition the broadening scheme of Methfessel and Paxton[26] and found that the influence of different broadenings on E_{1V}^F is smaller than 15 meV.

Table I represents our results for E_{1V}^F for different values of N, n_1, E_c, and various degrees of relaxation. It becomes obvious that the data are already well converged for $E_c = 12.5$ Ry. Going to $E_c = 16$ Ry changes E_{1V}^F by only few 0.001 eV. The data are also rather well converged already for $n_1 = 112$. Going to $n_1 = 330$ changes the values only by an amount of several 0.01 eV. The test of the convergence with respect to N for fixed n_1 is aggravated by the fact that the various supercells have different symmetries. Nevertheless, it appears that the results depend only weakly on N if we exclude the smallest supercell $(N = 8)$. Thereby the data with no relaxation and the data with total relaxation exhibit a very similar dependence on N, which shows that the convergence with respect to N is mainly determined by small electronic effects rather than by the even smaller elastic effects. Our guess is that the results for $N = 54$ differ by considerably less than 0.1 eV from the result which would be obtained for an infinitely large supercell. Altogether, we think that the residual uncertainty due to all convergence problems amounts to ± 0.1 eV. Taking the value of 2.895 eV for the totally relaxed $N = 54$ supercell at $n = 112$ for our best value, we arrive at $E_{1V}^F = (2.9 \pm 0.1)$ eV. For our feeling, the most reliable experimental data were obtained[27] by positron annihilation experiments, yielding (2.9 ± 0.3) eV from Doppler broadening experiments and (3.0 ± 0.2) eV from lifetime experiments. It becomes obvious that our result agrees very well with the experimental data, and the accuracy of our calculation probably (the systematic LDA error is hard to estimate) exceeds the accuracy of the experimental determination. It thereby should be noted that the experiments have been performed at high temperatures whereas the calculations are for zero temperature, so that the question of a possible temperature dependence of E_{1V}^F arises. Experimentally, however, there is no evidence for such a temperature dependence in the considered temperature regime ($T \gtrsim 2/3$ melting temperature). The FLMTO calculation of Ref. 15 was performed for $N = 27$, no structural relaxation was allowed and both the supercell with and without the vacancy were treated at the LDA lattice constant of perfect Mo. The obtained value for E_{1V}^F is 0.23 eV larger than our final value.

The structural relaxation of the atoms around the vacancy in Mo is rather small and has only a very weak influence on E_{1V}^F. It is of course largest for $N = 54$ where there are most structural degrees of freedom and results in a decrease of E_{1V}^F by about 0.08 eV. Former semiempirical calculations[28–31] also yielded relaxational energies of about 0.1 eV. This is a rather astonishing result. In Li[3] and Na[4] the relative decrease of E_{1V}^F due to structural relaxation is about a factor of 5 larger than in Mo. Whereas in Li there is an oscillatory relaxation pattern, in Mo all neighbors are slightly attracted for $N = 54$. The relaxation is strongest (about 1% of the original distance) for the next-nearest-neighbor shell, whereas for the nearest neighbors there is nearly no relaxation. The reason for this discrepancy between Li/Na and Mo is certainly the much larger ionic radius of Mo. Our results concerning the relaxation of the nearest- and next-nearest neighbors are in agreement with the data obtained by a most recently developed environment-dependent tight-binding model[31] and with those of a tight-binding bond model of Ohta[29] *et al.* In contrast, Xu and Moriarty[30] obtained by a multiatom interatomic potential derived from first-principles generalized pseudopotential theory an oscillatory displacement pattern, with an inward relaxation of -1.83% of the original distance to the vacancy for the nearest neighbors and an outward relaxation of 0.46% for the next-nearest neighbors. Common to all calculations is that the relaxations are small, except for the tight-binding study of Khanna *et al.*[32] which yields an inward (outward) relaxation of -6% (3%) for nearest neighbors (next-nearest neighbors). Obviously the results on the structural relaxations depend very sensitively on the details of the calculations.

According to Table I the effect of the volume relaxation on E^F_{1V} by going from the experimental lattice constant to the respective LDA equilibrium lattice constant of the supercell with and without the vacancy is considerably larger than the effect of the structural relaxation. It thereby should be noted that about half of the effect results from the fact that we started the calculation for the two supercells at the experimental lattice constant rather than at the LDA lattice constant of the perfect lattice. The second part results from the fact that the LDA lattice constant is different for the supercell with and without the vacancy, and from this difference the vacancy formation volume V^F_{1V} can be calculated (see above). For $N=54$, $n_1=112$, and $E_c=12.5$ Ry we obtained $V^F_{1V}=(0.6\pm0.1)\ \Omega_0$. (It should be noted that essentially the same value of V^F_{1V} was obtained for $N=16$ for various sets of n_1, E_c.) There is a large error of $\pm0.1\,\Omega_0$ because the dependence on the total energy of the supercell volume is rather weak, and it is therefore numerically difficult to locate the minimum of $E(V)$ accurately. For comparison, for Li and Na the LDA calculations[33] yielded a larger relaxation volume and hence a smaller vacancy formation volume of about $0.5\,\Omega_0$. By calculations based on empirical Finnis-Sinclair potentials[34] a value of $V^F_{1V}=0.73\,\Omega_0$ was found[35] for Mo. Experimentally, from a combined study of Huang diffuse scattering and changes of the lattice parameter in electron-irradiated Mo a range of $0.75\,\Omega_0 \leqslant V^F_{1V} \leqslant \Omega_0$ was estimated.[36]

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