Ab initio calculation of the formation and migration energies for monovacancies in Mg

H. Krimmel and M. Fähnle
Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany
(Received 7 March 2000; revised manuscript received 19 May 2000)

Within the framework of the density-functional theory in local-density approximation and the *ab initio* pseudopotential method a monovacancy formation energy E_{1V}^f of (0.83 ± 0.07) eV and migration energies E_{1V}^m of (0.47 ± 0.08) eV and (0.45 ± 0.08) eV are obtained for a vacancy-mediated self-diffusion along the *c* axis and in the basal plane of hexagonal Mg. The obtained migration energies fit to the experimental value obtained when assuming that the vacancy migrates in the resistivity recovery stage III. However, both the theoretical values for E_{1V}^f and E_{1V}^m as well as the experimental values (obtained by assuming a vacancy migration in stage III) add up to values for the activation energy of self-diffusion which are considerably smaller than the activation energy obtained by tracer self-diffusion experiments.

The investigation of the formation and migration properties of monovacancies in Mg is interesting for the following reasons.

(1) There are conflicting experimental results on the formation energy E_{1V}^f. The comparison of dilatometric and x-ray thermal expansion measurements at elevated temperatures lead to a rather low value of 0.58 eV.[1] The experiments were criticized by Tzanetakis *et al.*,[2] because the dilatometric and x-ray experiments were not performed for the same specimen. Indeed, electrical resistivity measurements at thermal equilibrium or after quenching yielded considerably larger values (see Ref. 2 and references therein), i.e., $E_{1V}^f = 0.79\pm0.03$ eV (Ref. 2) and $E_{1V}^f = 0.83\pm0.03$ eV (Ref. 3) when the measurements were performed under conditions of very low vacancy concentrations to prevent precipitation during the quench. Positron annihilation experiments in Mg are difficult to analyze: Because the binding energy E_b of a positron to a monovacancy in Mg is probably rather small,[4] a trapping-detrapping model has to be fitted to the experimental data, and the rather large number of fit parameters introduces an uncertainty for E_{1V}^f. For instance, assuming $E_b > 0.5$ eV yields $E_{1V}^f = (0.9\pm0.1)$ eV whereas for $E_b = 0.4$ eV the best fit is obtained for $E_{1V}^f = 0.85$ eV. An accurate *a priori* knowledge of E_{1V}^f would help to fix E_b. Altogether, the vacancy formation energy in Mg appears to be between 0.8 and 0.9 eV (if we omit the low value from the differential thermal dilatometry).

(2) There is a long-standing discussion on the interpretation of the various recovery stages upon annealing of irradiated or quenched metals which are denoted by numbers I to V (with stage I being subdivided into various substages), see, e.g., Refs. 5, 6. In the so-called one-interstitial model it is assumed that there are two elementary intrinsic point defects which exhibit long-range migration, the vacancy and the stable interstitial configuration, whereas in the two-interstitial model the vacancy, the stable interstitial configuration and a metastable interstitial configuration are considered for long-range migration. In the one-interstitial model stages I_E and III are attributed to the long-range migration of the stable interstitial configuration and of the vacancy, whereas in the two-interstitial model state I_E is associated with the migration of the metastable configuration, stage III with the migration of the stable configuration and stage IV with the migration of the vacancy. The two main recovery stages[6] in Mg are stage III and stage IV. Stage III is centered at about 130 K after neutron irradiation,[7] at slightly higher temperatures (130–170 K) after electron irradiation,[4,8] and it appears between 80 and 160 K after He^+ bombardment.[9] Stage IV appears around 215 K after quenching,[2] between 240 and 280 K after electron irradiation,[8] and between 200 and 280 K after He^+ bombardment.[9] The question under discussion again is whether the free migration of vacancies should be attributed to stage III (e.g., in Ref. 8) or stage IV (e.g., in Ref. 9). For a vacancy migration in stage III centered at about 130 K (Ref. 7) the migration energy E_{1V}^m would be about 0.45 eV. This value, however, is in conflict with the one obtained from $E_{1V}^m = E_{SD} - E_{1V}^f$ which is obtained when assuming that the self diffusion (and hence the activation energy E_{SD} for self-diffusion) is mediated by monovacancies. From the experimental value $E_{SD} = 1.44$ eV (Ref. 10) obtained by a tracer diffusion experiment, and inserting $0.8\text{ eV} \leqslant E_{1V}^f \leqslant 0.9\text{ eV}$, considerably larger migration energies, $0.54\text{ eV} \leqslant E_{1V}^m \leqslant 0.64\text{ eV}$, are found. The recovery at stage IV around 215 K found by Tzanetakis *et al.*[2] is consistent with a migration energy of 0.5 to 0.6 eV and hence compatible with the so obtained range of values for the migration energies. When judging all these numbers it should be taken into account that the various experimental data exhibit a statistical error and probably also a systematic error (for instance, related to a slight curvature of the Arrhenius plot for the self-diffusion data due to contributions of complex defects such as divacancies or to a temperature dependence of the defect properties). Therefore, it is not totally clear whether the discrepancy between $E_{1V}^f = 0.45$ eV found when attributing the vacancy migration to stage III and the larger values of the migration energy obtained from $E_{SD} - E_{1V}^f$ is really decisive.

(3) For hexagonal materials the diffusion tensor in general is anisotropic, and two migration energies $E_{SD}^{\parallel}$ for diffusion along the *c* axis and $E_{SD}^{\perp}$ for diffusion in the basal plane are expected. For Mg at most an extremely small anisotropy was found in the diffusion experiments,[10] with $E_{SD}^{\parallel} = 1.44$ eV and

$E_{SD}^{\perp}=1.43$ eV and with more or less identical preexponential factors. For comparison, in hexagonal Be there is indeed an anisotropy,[11] with $E_{SD}^{\parallel}=1.71$ eV and $E_{SD}^{\perp}=1.63$ eV.

In the present paper the energies of formation and migration of vacancies in Mg are calculated by the *ab initio* electron theory. There are only few *ab initio* calculations of the vacancy formation energy in hexagonal metals. The present authors considered the case of Be (Ref. 12) and Le Bacq *et al.*[13] the hexagonal phases of Ti, Zr, and Hf.

The calculations were performed within the framework of the density-functional theory in local-density approximation[14] and the *ab initio* pseudopotential method.[15,16] A supercell formalism is used, i.e., large supercells containing N sites and one vacancy were arranged periodically, and the formation energy was calculated from[17]

$$E_{1V}^{f}=E(N-1,1,\Omega')-\frac{N-1}{N}E(N,0,\Omega), \tag{1}$$

where $E(N-1,1,\Omega')$ is the energy of the supercell with $N-1$ atoms and one vacancy at the equilibrium volume Ω' and $E(N,0,\Omega)$ is the energy of the perfect supercell with N atoms at the equilibrium volume Ω. Both the ''structural relaxation,'' i.e., the individual relaxation of the atomic positions around the vacancy, and the ''volume relaxation,'' i.e., the change in the supercell volume due to the introduction of the vacancy, were taken into account. Due to the nonideal c/a ratio of Mg (see below) a vacancy in the basal plane has six nearest neighbors outside the basal plane with nearest-neighbor distance which is slightly smaller than a and six neighbors in the basal plane with distance a. The nearest neighbors of the vacancy exhibit an inward structural relaxation of 1%, the neighbors in the basal plane of 0.6%, the relaxations of all the other atoms are at least an order of magnitude smaller. The volume relaxation has only a negligibly small effect on E_{1V}^{f}, no matter whether we allow for an isotropic or an anisotropic (because of the hexagonal symmetry) change of volume due to the vacancy. The vacancy migration energy E_{1V}^{m} is calculated within the framework of the transition state theory[18] as the energy difference between two static, fully relaxed configurations, the first one with the moving atom in the saddle point configuration between the initial and the final state of the jump and the other one with the atom in the initial state. According to our experience for Li, Na, K, and Mo we assumed that the difference in volume for the supercell with the vacancy in the initial configuration and with the moving atom in the saddle point configuration has only a negligibly small effect on E_{1V}^{m}, and we therefore calculated the energy of the saddle-point configuration for the equilibrium volume of the initial configuration.

We considered all diffusion paths with jump distance $L \leqslant c$ (Fig. 1).

(1) Jump of an atom from the basal plane to a vacancy on a nearest-neighbor site in a parallel neighboring plane.

(2) Jump of an atom in the basal plane to a vacancy on the nearest-neighbor site in the same plane. The jump vector is slightly larger than for diffusion path 1, see above.

(3) Jump of an atom from the basal plane to a vacancy on the next-nearest-neighbor site in a parallel neighboring plane.

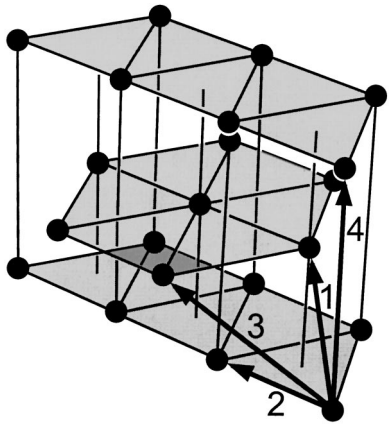

FIG. 1. The jump vectors for the four diffusion paths considered in this paper.

(4) Jump of an atom from the basal plane to a vacancy on the nearest-neighbor site along the c axis, i.e., the nearest-neighbor in a parallel next-nearest-neighbor plane.

Our calculations yielded $a=3.12$ Å, $c=5.06$ Å, and $c/a=1.62$. The experimental values are[19] $a=3.20280$ Å, $c=5.19983$ Å, and $c/a=1.62$ at 298 K.

The vacancy formation energy was calculated for supercells with $N=16$, 36, and 54 sites. For $N=54$ we obtained $E_{1V}^{f}=0.83$ eV with an estimated numerical error of ± 0.03 eV due to a nonperfect convergence of the results with respect to the supercell size and with respect to the number of plane waves used in the basis and the number of k points used for the sampling of the Brillouin zone. From the comparison[20] of *ab initio* data with the best experimental data for the case of other simple metals such as Li, Na, and Al we estimate the uncertainty resulting from the use of the local-density approximation to be smaller than 5%. The influence of nonlocal corrections to the local-density approximation has been investigated within the framework of the generalized-gradient approximation by Söderlind *et al.*[21] for the case of bcc transition metals. It turned out that there is only a weak influence on the vacancy formation energy for $4d$ and $5d$ metals and a stronger influence for $3d$ metals (especially Fe) with the strongly localized d states. We think that these nonlocal corrections are not important for Mg for which the valence states are much more free-electron-like. We thus finally obtain $E_{1V}^{f}=(0.83\pm 0.07)$ eV, whereby to our feeling the error limits have been chosen rather generously. This formation energy is consistent with the range of values $0.8 \leqslant E_{1V}^{f} \leqslant 0.9$ eV found experimentally, see above. It would fit to a binding energy of 0.4 eV between the positron and the vacancy, see above. The vacancy formation energy of Mg is smaller than the vacancy formation energy of Be, which is 1.13 eV.[12] For the vacancy formation volume $\Omega_{1V}^{f}=\Omega'-\Omega+\Omega_0$ we obtained $\Omega_{1V}^{f}=0.76\Omega_0$ where Ω_0 is the equilibrium atomic volume of the perfect material.

The vacancy migration energy first was calculated for a supercell containing 36 sites. We thereby assumed that the saddle-point configuration corresponds to the midpoint position of the jumping atom. For path 2 which turned out to be energetically most favorable one (see below) we have confirmed this assumption by an explicit calculation of the whole diffusion path. It turned out that for the diffusion paths

3 and 4 the migration energies are a factor of about 5 and 8 larger than for the diffusion paths 1 and 2. We therefore have redone the calculations for the diffusion paths 1 and 2 for a supercell containing 54 sites. Thereby the migration energies changed by less than 2%, i.e., we can assume that they are well converged with respect to the supercell size. We obtained $E_{1V}^m=(0.47\pm0.08)$ eV and $E_{1V}^m=(0.45\pm0.08)$ eV for diffusion path 1 and 2, where the estimated error limits (again generously chosen) encompass the numerical errors and the errors from the application of the local-density approximation. Because the diffusion path 1 exhibits a displacement along the *c* axis it may mediate a self-diffusion along the *c* axis with an activation energy of $E_{\mathrm{SD}}^{\parallel}$, whereas the diffusion path 2 with the slightly smaller migration energy will be favored for the diffusion in the basal plane, and we denote the corresponding activation energy with $E_{\mathrm{SD}}^{\perp}$. For the activation energies for self-diffusion via monovacancies $E_{\mathrm{SD}}=E_{1V}^f+E_{1V}^m$, we thus obtain $E_{\mathrm{SD}}^{\parallel}=1.3$ eV and $E_{\mathrm{SD}}^{\perp}=1.29$ eV. The calculations thus reproduce the experimental result that very similar activation energies are found for the diffusion along the *c* axis and in the basal plane, with $E_{\mathrm{SD}}^{\parallel}$ slightly larger than $E_{\mathrm{SD}}^{\perp}$.

Our values for E_{1V}^f, E_{1V}^m and $E_{\mathrm{SD}}=E_{1V}^f+E_{1V}^m$ are compared with experimental values in Table I. The calculated value of $E_{1V}^m=0.45$ eV fits to the experimental value of 0.45 eV which is obtained when assuming that the vacancy migrates in the recovery stage III. In spite of this clear statement, we want to mention that we run into the same problems as experimentalists when we try to understand not just one or the other experiment but all available experiments on the basis of this assignment. We just discuss two of these problems and refer to a critical discussion of all experiments in Ref. 6. First, if we take our values for E_{1V}^f and E_{1V}^m seriously, we end up with $E_{\mathrm{SD}}\approx(1.3\pm0.15)$ eV. The most probable value of 1.3 eV is considerably smaller than the experimental value of 1.44 eV. We therefore must conclude that either our error estimates for the calculation are too optimistic (although to our feeling they are already rather generously chosen) and that in reality the migration energy and/or the formation energy are larger than obtained by our calculations, or that the experimental value for the activation energy is too large. It therefore would be highly desirable to redo the diffusion experiment. Second, the fact that the recovery state IV occurs after quenching (where mainly vacancies are produced) is more naturally explained by assigning the vacancy migration to stage IV.

TABLE I. Comparison of theoretical results with experimental data (in eV). The experimental data for E_{1V}^m depend on the assignment of the vacancy migration to stage III or stage IV of the resistivity recovery, see text.

	Present Work	Experiment	
		stage III interpret.	stage IV interpret.
E_{1V}^f	0.83 ± 0.07	0.79–0.9 (Refs. 2–4)	
E_{1V}^m	$\begin{matrix}0.47\\0.45\end{matrix}\pm0.08$	0.45 (Ref. 7)	0.5–0.6 (Ref. 2)
$E_{1V}^f+E_{1V}^m$	1.30 ± 0.15	1.24–1.35	1.29–1.5
E_{SD}		1.44 (Ref. 10)	

[1] C. Janot, D. Malléjac, and B. George, Phys. Rev. B **2**, 3088 (1970).
[2] P. Tzanetakis, J. Hillairet, and G. Revel, Phys. Status Solidi B **75**, 433 (1976).
[3] P. Tzanetakis, Thése, Université des Grenoble, 1978.
[4] P. Hautojärvi, J. Johansson, A. Vehanen, and J. Yli-Kauppila, Appl. Phys. A: Solids Surf. **27**, 49 (1982).
[5] A. Seeger, Z. Naturforsch. A **10**, 251 (1955).
[6] W. Frank, J. Nucl. Mater. **159**, 122 (1988).
[7] J. Delaplace, J. Hillairet, J. C. Nicoud, D. Schumacher, and G. Vogl, Phys. Solid State **30**, 119 (1968).
[8] P. Vajda, F. Maury, A. Lucasson, and P. Lucasson, Radiat. Eff. **48**, 41 (1980).
[9] L. M. Howe, M. L. Swanson, and A. F. Quenneville, J. Nucl. Mater. **69 & 70**, 744 (1978).
[10] J. Combronde and G. Brébec, Acta Metall. **19**, 1393 (1971).
[11] N. L. Peterson, J. Nucl. Mater. **69 & 70**, 3 (1978).
[12] H. Krimmel and M. Fähnle, J. Nucl. Mater. **255**, 72 (1998).
[13] O. Le Bacq, F. Willaime, and A. Pasturel, Phys. Rev. B **59**, 8508 (1999).
[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[15] D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).
[16] B. Meyer, C. Elsässer, and M. Fähnle, FORTRAN 90 program for mixed-basis pseudopotential calculations for crystals, Max-Planck-Institut für Metallforschung, Stuttgart (unpublished).
[17] U. Breier, W. Frank, C. Elsässer, M. Fähnle, and A. Seeger, Phys. Rev. B **50**, 5928 (1994).
[18] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).
[19] M. E. Straumanis, J. Appl. Phys. **20**, 726 (1949).
[20] M. Fähnle, B. Meyer, J. Mayer, J. S. Oehrens, and G. Bester, in *Diffusion Mechanisms in Crystalline Materials*, edited by Y. Mishin *et al.*, MRS Symposia Proceedings No. 527 (Materials Research Society, Pittsburgh, 1998), p. 23.
[21] P. Söderlind, L. H. Yang, J. A. Moriarty, and J. M. Mills, Phys. Rev. B **61**, 2579 (2000).