

First-principles calculations of impurity diffusion activation energies in Al

Nils Sandberg and Randi Holmestad*

Norwegian University of Science and Technology (NTNU), Trondheim, Norway

(Received 10 May 2005; revised manuscript received 27 September 2005; published 20 January 2006)

We present first-principles density functional theory calculations of the diffusion activation energies of Mg, Si, and the 3*d* transition metals Sc–Zn in Al. In general, the calculated activation energies are underestimated with respect to experiments by 5–25%. The trend seen in experiments, namely, that impurities around Ti, V, and Cr have high diffusion activation energies leading to “anomalously” slow diffusion, is well reproduced in the present calculations. We provide an explanation in terms of electrostatic screening effects.

DOI: [10.1103/PhysRevB.73.014108](https://doi.org/10.1103/PhysRevB.73.014108)

PACS number(s): 66.30.Jt, 66.30.Dn, 66.30.Ny

I. INTRODUCTION

Atomic diffusion governs the rate of evolution toward metastable and stable phases in alloys. Impurity diffusion, representing the low-concentration limit of general interatomic diffusion, is of special theoretical and practical importance.^{1,2} In order to model chemical diffusion on an atomic level, this limiting case is important to understand.

First-principles density functional theory (DFT) calculations may provide detailed information about the mechanisms and energetics of diffusion. Such calculations have been applied to study self-diffusion,³ hydrogen diffusion,⁴ and substitutional impurity diffusion⁵ in metals. However, to connect experimentally measured diffusion parameters (prefactors and activation energies) to calculated parameters is not straightforward. Provided that the diffusion mechanisms are known, one has to account for quantum effects at temperatures below the Debye temperature, and anharmonic lattice vibrations at high temperatures. This, together with often substantial uncertainties in the measured diffusion data themselves, makes it difficult to judge the accuracy and usefulness of theoretical predictions.

In this paper, we present extensive first-principles DFT calculations of the diffusion activation energies (in short, diffusion energies) of Mg, Si, and the 3*d* transition metals (TM's) in Al. Our motivation for choosing these host and impurity systems is twofold. First, Al is a model material in solid-state physics and materials science. Well-established diffusion parameters exist for most impurities in this study; see a recent compilation in Ref. 6. Second, most of the impurities considered here are important alloying elements in commercial Al alloys, often in low concentrations. Therefore, their diffusion rates are of direct importance in the modeling of nucleation and growth processes in these materials.

The paper is organized as follows. The theory underlying the present calculations is summarized in Sec. II. In Sec. III, we first detail the calculations of the microscopic diffusion energies without spin polarization. Then, in separate calculations, the effects of spin polarization and of correlation in the atomic migration jumps are taken into account. In Sec. IV, the results are compared with available experimental data, and finally we discuss the trend in the diffusion energies over the TM series and compare to that in a recent similar study of TM impurity diffusion in Ni.⁵ Conclusions are drawn in Sec. V.

II. CALCULATIONAL DETAILS

For vacancy-mediated diffusion, the diffusion rate D at temperature T is given by¹

$$D = D_0 f \exp[-(H_{IV} + H_I^m)/k_B T] \quad (1)$$

where D_0 is a prefactor with dimension length² per unit time, f is the correlation factor (see below), and k_B is the Boltzmann constant. H_{IV} denotes the energy of forming a vacancy next to an impurity (the vacancy formation energy minus the impurity-vacancy binding energy) and H_I^m is the impurity migration energy.

In the classical approximation, and assuming harmonic lattice vibrations, H_{IV} may be calculated from

$$H_{IV} = E_{IV}^{\text{tot}}(\text{Al}_{N-2}, I, V) - E_I^{\text{tot}}(\text{Al}_{N-1}, I) + \frac{1}{N} E_B^{\text{tot}}(\text{Al}_N) \quad (2)$$

where N is the number of lattice points (LP's), and $E_{IV}^{\text{tot}}(\text{Al}_{N-2}, I, V)$, $E_I^{\text{tot}}(\text{Al}_{N-1}, I)$ and $E_B^{\text{tot}}(\text{Al}_N)$ are the total energies of the fully relaxed impurity-vacancy [Fig. 1(a)], impurity, and bulk systems, respectively. The structural relaxation includes the volume and shape of the supercell.

The impurity migration energy is similarly given by

$$H_I^m = E_{TS}^{\text{tot}}(\text{Al}_{N-2}, I, V) - E_{IV}^{\text{tot}}(\text{Al}_{N-2}, I, V) \quad (3)$$

where $E_{TS}^{\text{tot}}(\text{Al}_{N-2}, I, V)$ is the energy of the unstable transition state (TS) in Fig. 1(b). Again, all coordinates (except the unstable reaction coordinate) are fully relaxed. This gives for the “microscopic” diffusion energy $H^D \equiv H_{IV} + H_I^m$

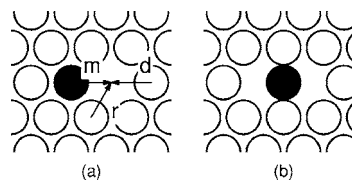


FIG. 1. A $\{111\}$ plane of atoms illustrating atomic migration steps relevant for impurity diffusion in fcc crystals. (a) Impurity migration is denoted m , impurity-vacancy reorientation is denoted r , and impurity-vacancy dissociation is denoted d . (b) The transition state of the impurity migration process.

TABLE I. Convergence of impurity diffusion energies with respect to k -point density and supercell size. The energies (in eV) refer to GGA calculations.

	$N=64$ $4 \times 4 \times 4$	$N=64$ $5 \times 5 \times 5$	$N=64$ $6 \times 6 \times 6$	$N=125$ $4 \times 4 \times 4$
Cr	2.42	2.35	2.37	2.40
Cu	1.02	0.95	0.99	1.03
Al	1.04	0.91		

$$H^D = E_{\text{TS}}^{\text{tot}}(\text{Al}_{N-2}, I, V) - E_I^{\text{tot}}(\text{Al}_{N-1}, I) + \frac{1}{N} E_{\text{B}}^{\text{tot}}(\text{Al}_N). \quad (4)$$

It is seen that the impurity-vacancy state is an intermediate step whose energy cancels in the calculation of the total diffusion energy.

We have calculated H_{IV} and H_I^{m} using the DFT method as implemented in the program VASP.⁷ It uses plane waves and pseudopotentials to describe the electronic structure of the system. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) by Perdew and Wang⁸ were used to account for the exchange-correlation energy.

Most calculations were done using a $5 \times 5 \times 5$ k -point mesh in a 64 LP supercell. Inspection of Table I reveals that this choice of k -point mesh seems to systematically underestimate the diffusion energy. Due to limited computer resources, we have retained the $5 \times 5 \times 5$ grid, keeping in mind that a 0.05–0.15 eV shift up in H^D is expected.

III. RESULTS

Figure 2 shows the resulting H_{IV} and H^D for Si, Mg, and Sc–Zn in Al using nonmagnetic calculations and ultrasoft pseudopotentials.⁹ It is seen that the GGA underestimates H_{IV} and H^D with respect to the LDA values. This is related to electronic edge effects and may in principle be compensated for.^{3,10,11}

The effect of spin polarization of the TM impurities Ti–Ni needs extra consideration. It was calculated separately using

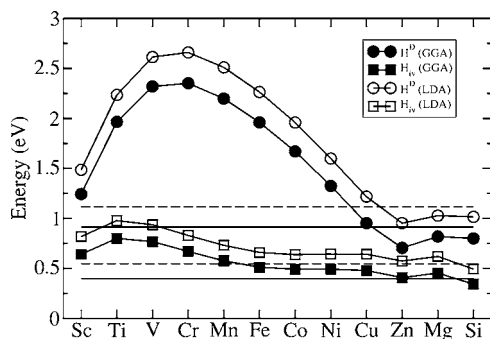


FIG. 2. Calculated microscopic impurity diffusion energies H^D . The impurity-vacancy formation energy is also shown. Horizontal lines show the Al vacancy formation (lower lines) and self-diffusion (upper lines) energies, calculated using the GGA (solid) or LDA (dashed) exchange-correlation approximations.

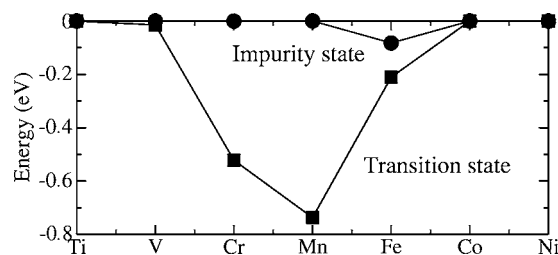


FIG. 3. The energy difference between spin-polarized and non-spin-polarized calculations of the impurity and transition states, respectively.

the “projector augmented wave” pseudopotentials.¹² Using a $2 \times 2 \times 2$ k -point mesh, 108 LP systems were relaxed in non magnetic calculations. Then, spin-polarized calculations were carried out for volumes of the corresponding nonmagnetic systems (thus neglecting the “magnetic stress”). It is seen in Fig. 3 that spin polarization decreases the diffusion energy for the impurities Cr, Mn, and Fe. Calculations have revealed a similar effect for the activation energies of the $3d$ TM’s in Ni.⁵

The development of spin-polarized solutions was very sensitive, e.g., to the initial atomic structure. In general, the spin polarization disappeared if the four nearest-neighbor Al atoms were too close to the TM impurity in the TS. We therefore expanded the lattice slightly before the relaxation. In Co for example, a spin moment was initially present, but was out-balanced by the ionic relaxation, which lowered the elastic energy of the system.

The magnetic moment of TM impurities in Al bulk and clusters has been extensively studied both experimentally and theoretically (see Refs. 13 and 14 and references therein). It depends sensitively both on the local structure (the distance from the impurity to the nearest-neighbor Al atoms) and on the total volume. The present calculations show that one may expect this effect to be even more pronounced for the TM impurity at the transition state. We therefore regard this as a suitable area for future, more systematic studies.

Next, we consider the correlation factor f in Eq. (1). Its effect on the effective macroscopic diffusion energy, as it is measured in tracer diffusion experiments, is seen by differentiating Eq. (1),

In order to calculate f , as a function of temperature, we make use of the five-frequency model.² It neglects impurity-vacancy interactions beyond first nearest neighbors, an assumption that may be questionable in Al.¹⁵ However, we have retained this first level of approximation. The correlation factor is then given by (for a fcc lattice)

$$f = \frac{\omega_r + \omega_d F(\omega_a/\omega_0)/2}{\omega_m + \omega_r + \omega_d F(\omega_a/\omega_0)/2} \quad (6)$$

where ω_r , ω_d , and ω_m are jump frequencies of the reorientation, dissociation, and migration steps indicated in Fig. 1. ω_0 is the host atom migration frequency and F is a function of ω_a/ω_0 where ω_a is the *association* step. We used $F(1) = 5.15$.² We calculated all relevant jump frequencies ω

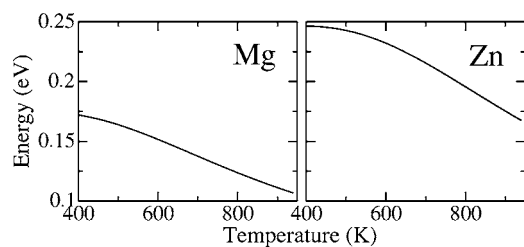


FIG. 4. The effective energy barrier $-d \ln f/d(1/k_B T)$ for Mg and Zn [see Eq. (5)]. The results were obtained by numerical differentiation of Eq. (6).

$= \nu_0 \exp(-H/k_B T)$ as follows. The atom migration energies H were calculated in 32 lattice-point cells using $4 \times 4 \times 4$ k points.¹⁶ The corresponding attempt frequencies ν_0 were estimated using the commonly occurring linear relation between activation energies H and the logarithm of the microscopic prefactor, $\ln \nu_0 = a + bH$. Based on calculated point-defect migration parameters in Al we used $b = 4.89 \text{ eV}^{-1}$.¹¹ It is interesting to note that the corresponding empirical constant for impurity diffusion in Al is $b = 6.22 \text{ eV}^{-1}$.⁶

For the TMs, where H_I^m is large compared with the dissociation step, $f \approx 1$ because it is more likely that a migration step is followed by dissociation than by a new migration step. In this case, the next migration step requires binding to a new vacancy, and it will be uncorrelated with the previous jump. This means that $d \ln f/d(1/k_B T) \approx 0$. In the case of Mg and Zn, there is a transition from correlated to more uncorrelated impurity jumps over the temperature interval of interest leading to a finite $d \ln f/d(1/k_B T)$ (see Fig. 4).

Adding up the diffusion energies in Fig. 2 and the corrections due to spin polarization and correlation effects, we obtain the total effective diffusion energies $H^{D,\text{calc}}$. They are plotted in Fig. 5 together with the available experimental data. It is seen that the general feature, namely, the increased diffusion energies around Ti, V, and Cr, is well reproduced in our calculations. This is largely due to a corresponding strong variation in the impurity migration energies H_I^m . The variation in the impurity-vacancy formation energy is smaller by a factor of 4–5. Therefore, the explanation for the anomalously slow diffusion of Ti–Fe should be sought not in the impurity-vacancy formation energy but in the impurity migration energy.

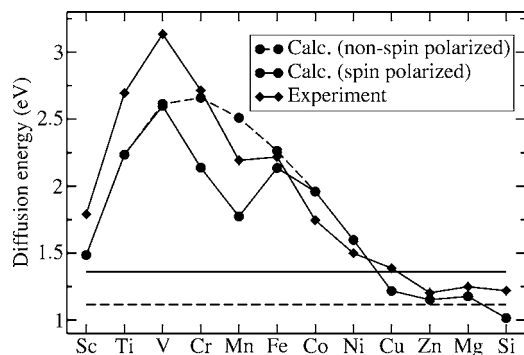


FIG. 5. Calculated macroscopic diffusion energies compared to experimental energies (from Refs. 1, 6, and 17).

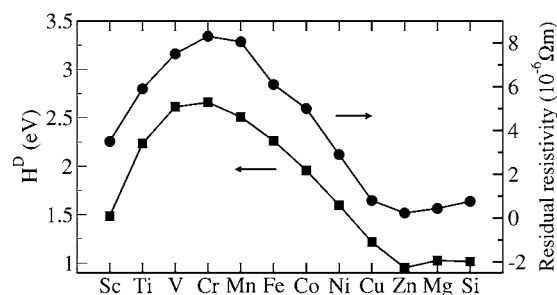


FIG. 6. The nonmagnetic diffusion energies from Fig. 2 (squares) and the residual resistivity per unit concentration of impurities in Al (circles), (Ref. 23) taken from Ref. 24.

IV. DISCUSSION

Among the experimental impurity diffusion activation energies in Fig. 5, we regard Cr, Mn, Fe, Co, Cu, Zn, Mg, and Si to be more accurate than the others (see Refs. 6 and 18). With the exception of Co and Fe, they are 5–25% higher in energy than the calculated energies. It is known from simulations, in the case of Cu and Al, that anharmonic lattice vibrations lead to an increase in defect formation and migration energies.^{3,11,19} In the case of Al, the increase in H^D is about 10–15%. We find it plausible that a similar increase in the effective diffusion energies is present in the case of impurity diffusion in Al. However, to actually calculate this effect is difficult, since it stems from explicit anharmonic terms.²⁰ Such a calculation therefore requires the use of model potentials for each host-impurity system in question.

The situation with Co is reversed; the diffusion activation energy is *overestimated* by 15% compared with the experimental value. From different sets of experiments¹⁸ we estimate $H^{D,\text{exp}}$ to $1.80 \pm 0.1 \text{ eV}$, i.e., clearly below our calculated energy. Considering the trends in Fig. 5, one may suspect that there is a lowering of the Co diffusion energy due to spin polarization at the TS, but in our calculations we have not been able to find such a solution.

In a recent paper, Janotti *et al.*⁵ present first-principles calculations of TM impurity diffusion energies in Ni. They find an inverse relation between the atomic radius and the diffusion energy, i.e., larger atoms diffuse faster than smaller atoms, and argue that this should hold also for impurity diffusion in other metals. The case of 3d impurity diffusion is complicated by the effect of magnetism, but it is still instructive to contrast the present study with that of Janotti *et al.* Among the 3d transition metals, Mn, Fe, Co, and Ni have the smallest radii, while the slowest diffusers (with the highest activation energies) in Al are Ti, V, and Cr as seen in Fig. 5. The reason for this difference is most likely that Al, unlike Ni, is a free-electron-like metal. For such hosts, the electrostatic interaction between an impurity atom and a vacancy, acting effectively as a positive point charge, has been related to H^D in the so-called half-vacancy model.² Our preliminary calculations show that this model is of limited value in explaining the trends in Al. However, we note the striking similarity between the variations in the residual resistivity and the diffusion energies, as a function of valence (see Fig. 6). The residual resistivity is in turn related to the scattering of

TABLE II. Chemical energies and elastic energies (in eV) associated with the impurity and transition states, respectively. See text for further details.

	$\Delta E_{\text{TS}}^{\text{chem}}$	ΔE_I^{chem}	$\Delta E^{\text{D,chem}}$	$\Delta E_{\text{TS}}^{\text{str}}$	ΔE_I^{str}	$\Delta E^{\text{D,str}}$
Sc	-6.18	-6.51	0.34	0.36	0.11	0.25
Cr	-7.29	-8.80	1.51	0.18	0.03	0.15
Fe	-7.46	-8.66	1.20	0.28	0.08	0.20
Zn	-1.69	-1.78	0.10	-0.02	-0.01	-0.00

electrons by a screened impurity ion.^{2,21} This nontrivial correlation therefore indicates two things. One is that electrostatic effects play a major role for the diffusion energies in Al. The other is that the diffusion energy depends on the impurity state itself because the efficiency of electron scattering on impurities, *generally in the absence of vacancies*, is correlated with the activation energy of *vacancy-assisted* diffusion.

Further insight can be gained by considering the chemical energy ΔE^{chem} , defined here as the energy of the relaxed host+impurity system (E_I^{tot}) minus the sum of the energies of the host matrix only (at the same ionic positions), and the impurity atom. Table II shows ΔE^{chem} for the impurity state and the transition state for Sc, Cr, Fe, and Zn. There is a large lowering in energy due to the promotion of the valence electrons to the conduction band (compare, e.g., to total energies calculated in Ref. 22). This leaves the impurity ion as an effective point charge. Further energy lowering is therefore possible through screening of the impurity. This mechanism is less effective in the TS, because the ion is partly surrounded by electronic voids. Therefore

$$\Delta E^{\text{D,chem}} \equiv \Delta E_{\text{TS}}^{\text{chem}} - \Delta E_I^{\text{chem}} \quad (7)$$

becomes large and positive for TM's in the middle, with a shift to the left, in the 3d series.

We also calculated the corresponding strain energy associated with the impurity and transition states as the total energy of the Al matrix without the impurity, relative to the unstrained corresponding systems. The variation in

$$\Delta E^{\text{D,str}} \equiv \Delta E_{\text{TS}}^{\text{str}} - \Delta E_I^{\text{str}} \quad (8)$$

is much smaller than the variation in $\Delta E^{\text{D,chem}}$, showing that chemical effects rather than strain effects explain the trend in Fig. 2.

V. CONCLUSIONS

In conclusion, we have presented extensive calculations of impurity diffusion activation energies in Al. The large activation energies for the impurities around Ti, V, and Cr are a consequence of large impurity migration energies for these elements. We relate this to reduced screening of the impurity at the transition state. Spin polarization decreases H^D for Cr and Mn substantially (-0.75 eV for Mn). The agreement between the present calculations and measured activation energies in the literature is generally good. The systematic deviation, with $H^{D,\text{expt}}/H^{D,\text{calc}}$ typically within 1.1–1.2, may at least partly be due to the neglect of anharmonic lattice vibrations in our calculations.

ACKNOWLEDGMENTS

We thank A. Ruban and G. Grimvall for helpful discussions. This work was supported by the Research Council of Norway (the program for supercomputing and Contract No. 140553/I30).

*Electronic address: randi.holmestad@phys.ntnu.no

¹H. Mehrer, N. Stolica, and N. A. Stolwijk, in *Diffusion in Solid Metals and Alloys*, edited by H. Mehrer, Landolt-Börnstein, New Series, Group III, Vol. 26 (Springer-Verlag, Berlin, 1990).

²A. D. le Claire, *J. Nucl. Mater.* **78**, 70 (1978).

³K. Carling, G. Wahnström, T. R. Mattsson, A. E. Mattsson, N. Sandberg, and G. Grimvall, *Phys. Rev. Lett.* **85**, 3862 (2000).

⁴D. E. Jiang and E. A. Carter, *Phys. Rev. B* **70**, 064102 (2004).

⁵A. Janotti, M. Krčmar, C. L. Fu, and R. C. Reed, *Phys. Rev. Lett.* **92**, 085901 (2004); M. Krčmar, A. Janotti, C. L. Fu, and R. C. Reed, *Acta Mater.* **53**, 2369 (2005).

⁶Y. Du, Y. Chang, B. Huang, W. Gong, Z. Jin, H. Xu, Z. Yuan, Y. Liu, Y. He, and F.-Y. Xie, *Mater. Sci. Eng., A* **363**, 140 (2003).

⁷G. Kresse and J. Hafner, *Phys. Rev. B* **47**, R558 (1993); **49**, 14251 (1994); G. Kresse and J. Furthmüller, *ibid.* **54**, 11169 (1996).

⁸J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992); **48**, 4978(E) (1993).

⁹D. Vanderbilt, *Phys. Rev. B* **41**, R7892 (1990); G. Kresse and J. Hafner, *J. Phys.: Condens. Matter* **6**, 8245 (1994).

¹⁰T. R. Mattsson and A. E. Mattsson, *Phys. Rev. B* **66**, 214110 (2002).

¹¹N. Sandberg, B. Magyari-Köpe, and T. R. Mattsson, *Phys. Rev. Lett.* **89**, 065901 (2002).

¹²P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).

¹³F. Lechermann, M. Fähnle, B. Meyer, and C. Elsässer, *Phys. Rev. B* **69**, 165116 (2004).

¹⁴L. I. Kurkina, O. V. Farberovich and V. A. Gorbunov, *J. Phys.: Condens. Matter* **5**, 6029 (1993).

¹⁵P. A. Sterne, J. van Ek, and R. H. Howell, *Comput. Mater. Sci.* **10**, 306 (1998).

¹⁶In the case of impurity-vacancy splitting, the initial and final states are unequal, and consequently the state with the impurity atom half way between those states is not symmetric. We estimated the TS energy by relaxing all coordinates until the reaction coordinate started to grow. The energy thus obtained is not the exact TS energy, but an acceptable approximation.

¹⁷E. Clouet, M. Nastar, and C. Sigli, *Phys. Rev. B* **69**, 064109 (2004).

¹⁸G. Rummel, T. Zumkley, M. Eggersmann, K. Freitag, and H.

- Mehrer, Z. Metallkd. **86**, 122 (1995).
- ¹⁹N. Sandberg and G. Grimvall, Phys. Rev. B **63**, 184109 (2001).
- ²⁰G. Grimvall, *Thermophysical Properties of Materials*, enlarged and revised ed. (Elsevier, Amsterdam, 1999).
- ²¹M. S. Anand and R. P. Agarwala, Philos. Mag. **26**, 297 (1972).
- ²²Y. Wang, S. Curtarolo, C. Jiang, R. Arroyave, T. Wang, G. Ceder, L.-Q. Chen, and Z.-K. Liu, CALPHAD **28**, 79 (2004).
- ²³The residual resistivities contain a contribution from the volume change of alloying, which in turn affects the resistivity. Based on the pressure dependence of the resistivity in Al, we estimate this effect to be within $\pm 0.1 \times 10^{-6} \Omega \text{ m}$.
- ²⁴J. Bass, in *Metals: Electronic Transport Phenomena*, edited by K.-H. Hellwege and J. L. Olsen, Landolt-Börnstein, New Series, Group III, Vol. 15, Pt. A (Springer-Verlag, Berlin, 1982).