Solute Diffusion in Metals: Larger Atoms Can Move Faster

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First-principles calculations for the diffusion of transition metal solutes in nickel challenge the commonly accepted description of solute diffusion rates in metals. The traditional view is that larger atoms move slower than smaller atoms. Our calculation shows the opposite: larger atoms, in fact, can move much faster than smaller atoms. Conventional mechanisms involving the effect of misfit strain or the solute-vacancy binding interactions cannot explain this counterintuitive diffusion trend. Instead, the origin of this behavior stems from the bonding characteristics of the d electrons of solute atoms, suggesting that a similar diffusion trend also occurs in other types of host lattices.

The rate of atomic diffusion in solids governs the kinetics of microstructural changes and processes of mass transport at elevated temperatures. In this paper, we challenge a commonly accepted view regarding the diffusion of substitutional solute atoms in metallic matrices. Namely, in considering the diffusion of solute atoms in a given host lattice, it is commonly believed (for example, see Ref. [1]) that the larger the solute atom, the slower its diffusion rate. This belief is based on the consideration of lattice strain induced by diffusing atoms, which increases as the size misfit between the host and the solute atoms increases. Thus, in terms of the misfit strain, the work required to overcome the diffusion barrier for large atoms is often thought to greatly exceed that of small atoms. This long-accepted view will be critically examined by our first-principles calculations.

Here, we consider the diffusion of transition metal (TM) solutes in a host Ni lattice. Since Ni has a close-packed lattice with a small lattice parameter, it is an ideal system for studying the effect of size misfit between solute and solvent atoms on the diffusion. The choice of Ni as the host lattice is also motivated by the puzzling experimental observations for the diffusion of $4d$ and $5d$ TM solutes. An analysis on the experimental data for the diffusion rates of selected $4d$ and $5d$ TM solutes in Ni [2–9] shows a surprising result: solute atoms with atomic radii closest to that of Ni display the slowest diffusion rates. As pointed out by Karunaratne and Reed [2], there is a possible correlation between the diffusion coefficient and the magnitude of atomic radius: the larger the solute, the faster its diffusion rate. The scientific basis for such a correlation is not at all understood.

The solute atoms under consideration in our calculations not only include the nonmagnetic $4d$ and $5d$ series but also extend to the magnetic $3d$ series. We prove the unexpected trend: larger atoms can indeed move much faster than smaller atoms. And even more surprisingly (and contrary to common belief), the effect of misfit

lattice strain is found to play only a minor role in the observed trend. The origin of the diffusion trend lies in the characteristics of the d-states occupancy in the electronic structure of solute atoms; the development of bonding directionality in the d states leads to lower compressibility and higher diffusion energy barriers. While this study is limited to the diffusion of TM solutes in Ni, the identified characteristics of the diffusion mechanism are general and should be applicable to other types of host lattices.

We solve the density-functional equations in the local density approximation (LDA) [10] using the ultrasoft pseudopotential method [11,12]. A 32-atom supercell represents the host nickel lattice, with one Ni atom replaced by a TM solute atom. Convergence tests were performed for the solute-vacancy binding energies and diffusion energy barriers for both the $4d$ and $5d$ TM solutes by increasing the size of the supercell; calculations with a 64-atom supercell yield the same results as for the 32-atom supercell (to within less than 1%).

In the face-centered-cubic (fcc) structure, the diffusion of the substitutional solute atoms is mediated by the adjacent lattice vacancies [1]. The diffusion activation energy (Q) can be written as a sum of the diffusion energy barrier (E_b) and the vacancy formation energy adjacent to a solute (E_f^V). Here E_f^V is given as the sum of the vacancy formation energy of the host and the solute-vacancy binding energy. The diffusion energy barrier is calculated by displacing a solute atom towards the adjacent vacancy along the $\langle 110 \rangle$ direction in the fcc lattice. As a benchmark, we calculated the energy barrier for self-diffusion and the vacancy formation energy in Ni. We obtained 120 and 164 kJ/mol for the diffusion energy barrier and the vacancy formation energy, respectively. The calculated activation energy is 284 kJ/mol, in good agreement with the experimental value of 285 kJ/mol [13]. Figure 1(a) shows the results for the calculated diffusion activation energy of the $4d$ and $5d$ solutes in Ni, and
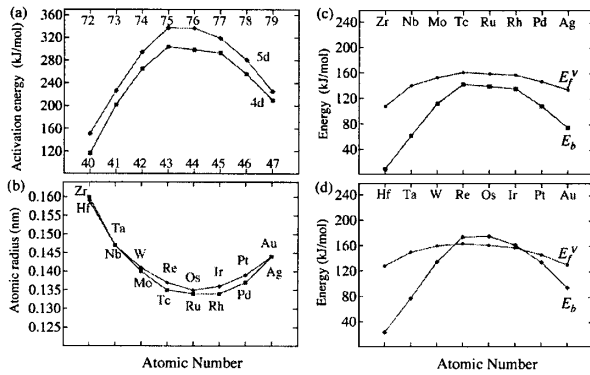
FIG. 1.   (a) Dependence of the diffusion activation energy (Q) on atomic number for $4d$ and $5d$ TM solutes in Ni. (b) The size of the atomic radii (i.e., Goldschmidt radii [14]) for both the $4d$ and the $5d$ series. Contributions from the vacancy formation energy adjacent to a solute (E_f^V) and the diffusion energy barrier (E_b) to Q for the $4d$ and $5d$ TM solutes in Ni are in (c) and (d).

Fig. 1(b) displays the size of the atomic radii (i.e., Goldschmidt radii [14]) of these solutes. These results are truly remarkable, considering that the activation energy varies across the TM series in a counterintuitive way: larger atoms (early and late TM elements) have lower diffusion activation energies than smaller atoms (middle TM elements). The individual contributions from E_f^V and E_b are shown in Figs. 1(c) and 1(d). The E_f^V term follows the expected trend: the larger the misfit between solute and solvent atoms, the larger (or more negative) the solute-vacancy binding energy. However, compared to the diffusion energy barrier, the solute-vacancy binding energy shows only a weak dependence on the atomic number of the solutes. The major contribution to the variation of the activation energy comes from the variation of the diffusion energy barrier across the $4d$ and $5d$ TM series.

We find that there is good agreement between theory (164 kJ/mol or 1.7 eV) and experiment [15] (1.7 ± 0.1 eV) in the vacancy formation energy of Ni. The agreement, however, may be fortuitous, since the work by Mattsson [16] suggests that LDA calculations tend to underestimate the vacancy formation energy of selected transition metals by 0.1–0.2 eV. Nevertheless, in the present case, any intrinsic LDA error in the vacancy formation energy would imply a small rigid shift in the diffusion activation energy across the TM series and should not affect the overall calculated diffusion trends.

We note that the activation energy of the $5d$ solutes is systematically higher than that of the $4d$ solutes, even though the isoelectronic $4d$ and $5d$ elements have nearly identical atomic radii. We will show that the trend in the diffusion energy barrier can be described by the compressibility of solute elements. Since the magnitude of the compressibility manifests the size of the atomic radius within a TM series, it becomes possible to establish a correlation between atomic radius and diffusion activation energy across a TM row.

In the following discussion, we focus on the $5d$ solutes. For vacancy-mediated diffusion, the diffusion coefficient of the diffusing solute atom at temperature T is

$$D = fD_0 e^{-Q/k_B T}, \qquad (1)$$

where f is the correlation factor, D_0 is the prefactor [17], and k_B is the Boltzmann constant. The correlation factor, which takes into account the fact that the diffusing atom can jump back to its previous lattice site if the solute-vacancy pair remains undissociated, can be approximated from the Lidiard's five-frequency exchange model as [1]

$$f \cong \frac{2\Gamma_1 + 7\Gamma_2}{2\Gamma_s + 2\Gamma_1 + 7\Gamma_2}, \qquad (2)$$

where Γ_1 and Γ_2 are the rates of site exchange between vacancy and host atom that results in the rotation and dissociation of a solute-vacancy pair, respectively, and Γ_s is the rate of site exchange between vacancy and solute. These site-exchange rates can be obtained from the diffusion energy barriers. For early and late $5d$ TM solutes, we find that $\Gamma_2 > \Gamma_1$; the site-exchange energy barrier in the Γ_2 term differs insignificantly (to within 10 kJ/mol) from that of Ni self-diffusion and is about 40 kJ/mol lower than that in the Γ_1 term. The calculated correlation factors are of the order of 10^{-3} for Hf and 10^{-1} for Au at 1000 °C. For midrow TM solutes, we find that $\Gamma_1 \cong \Gamma_2 \gg \Gamma_s$, yielding $f \cong 1$ (the energy barrier in both the Γ_1 and Γ_2 terms is about 115 kJ/mol for the Re solute). The migration entropy contribution in the prefactor D_0 [17] can be estimated by considering the vibration degrees of freedom of the migrating solute atoms as given by a collection of classical harmonic oscillators. Under these assumptions, the solute atoms are displaced in three orthogonal directions, and the vibration frequencies are evaluated through the calculated force constant matrices. For $5d$ solutes in Ni, the prefactors D_0 are found to be of the order of 10^{-5} m^2 s^{-1}. The calculated diffusivity of these solutes shown in Fig. 2 is in good agreement with experiments [2] in both the trends and the magnitudes
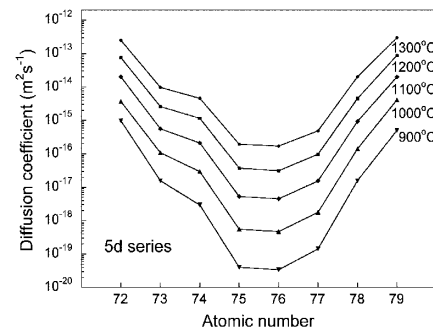

FIG. 2.   Calculated diffusion coefficient (D) for $5d$ transition metal solutes in Ni at various temperatures.

across the 5d series. Note that the diffusion coefficients of the midrow TM solutes are several orders of magnitude smaller than those of the early and late TM solutes.

When inserted into the host lattice, larger solute atoms induce larger lattice strain. Intuitively, one would expect that a larger strain field leads to a higher diffusion energy barrier. However, one should keep in mind that the diffusion energy barrier is the energy difference between the solute atom at the lattice site and at the saddle point; therefore, it is the difference in strain between these two lattice configurations that contributes to the energy barrier. The difference in strain will be manifest in the change of the interatomic distances. We find that the contraction in the nearest neighbor distance (between solute and Ni) from solute at the lattice site to solute at the saddle point displays only a weak dependence on the atomic size of the solutes, e.g., the amount of contraction is 6.8% (0.17 Å), 6.2% (0.15 Å), and 5.6% (0.14 Å) for Hf, Re, and Au solutes, respectively. Therefore, in terms of the effect of misfit strain on the diffusion energy barrier, there is no significant difference between larger and smaller solute atoms.

Figure 3 shows the valence charge density of Hf, Re, and Au solutes, representing the variation of the chemical bond across the 5d row, in the (001) planes of the Ni host lattice. It indicates that (i) the d electrons of Hf do not participate in directional bonding with its nearest neighbor Ni atoms; (ii) the charge density of Re exhibits a clear orientation along the $\langle 110 \rangle$ directions with Ni as the nearest neighbors, indicating the development of directional d bonds; and (iii) the Au d electrons are highly localized and chemically inactive due to its closed d shell. In analogy to the case of the elemental TM series, one expects an increase of the attractive partial pressure due to the directional bonding developed within the d states for the midrow 4d and 5d TM solutes. Meanwhile, the s-electron contribution to the partial pressure experienced by these elements has to become more repulsive (and thus the radius correspondingly smaller) in order to counterbalance this attractive d-electron partial pressure to achieve equilibrium. As a result, the equilibrium Re-Ni interatomic distance is among the smallest across the 5d row. On the other hand, the rapid increase in the s-electron

partial pressure at a smaller radius is reflected in a low compressibility for smaller solutes.

Since solute atoms are considerably compressed near the saddle point, the diffusion energy barrier should reflect the degree of bonding directionality of the solutes. To further show that smaller solute atoms are indeed more difficult to compress, we carried out a model calculation to examine the trend in the 5d solute compressibility due to the change of local pressure exerted by neighboring host atoms. With solutes located at the lattice site, we displace the nearest neighbor Ni shell uniformly towards the solutes but allow the rest of the host Ni atoms to relax. The resulting strain energy is found to differ considerably among different solutes; it is the highest for Re but the lowest for Hf, even though Hf is already more prestrained before compression. In other words, the presence of directional bonds makes the midrow solutes less compressible than the early and late TM solutes in the 4d and 5d TM series—a trend consistent with the trend in the compressibility of elemental transition metals [18].

We find that the compressibility of elemental transition metals provides a comprehensive physical basis to describe the trend in the diffusion energy barrier of TM solutes. The fact that the solute elements with lower compressibility also have smaller atomic radii leads to the "counterintuitive" correlation between atomic radius and diffusion activation energy across a TM series. Moreover, the fact that the diffusion energy barriers in the 5d TM series systematically exceed those in the 4d TM series (Fig. 1) is largely due to lower compressibility for the 5d elements. However, a direct comparison of the diffusion energy barriers between 3d and 4d/5d solutes cannot be fully established solely on the basis of the compressibility of elemental transition metals due to the complexity of the magnetic coupling between 3d solutes and Ni (see below).
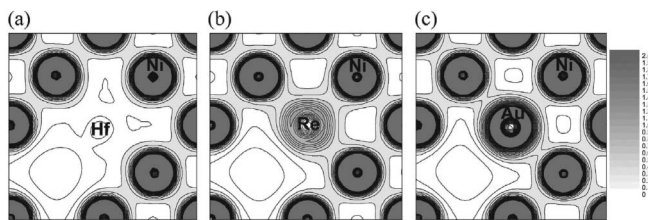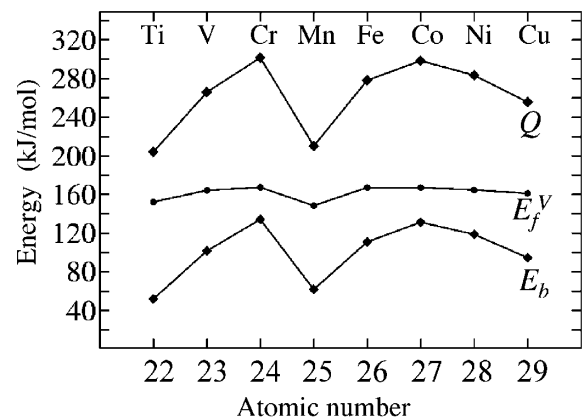

FIG. 3. Electronic charge density (in units of $e/\text{Å}^3$) of (a) Hf, (b) Re, and (c) Au solutes in the (001) plane of the fcc Ni lattice. Note that a vacancy is located next to the solute atom.

FIG. 4. Dependence of the diffusion activation energy (Q), the vacancy formation energy adjacent to a solute (E_f^V), and the diffusion energy barrier (E_b) on atomic number for 3d solutes in Ni.

We now turn to the diffusion of 3d solutes in Ni. Note that the size misfit with the host is less pronounced for the 3d solutes; thus the system under study is different from the diffusion of larger solute atoms in a smaller lattice. Our calculations show that the activation energy of the 3d solutes (Fig. 4) displays an even more complex and intriguing dependence on the atomic number. Similar to the case of the 4d and 5d solutes, the solute-vacancy binding energy exhibits a weaker dependence on the atomic number than the diffusion energy barrier across the 3d row. But, very unlike the case of the 4d and 5d solutes, a local minimum in the diffusion energy barrier profile is found to exist in the middle of the 3d TM series (i.e., at the position of the Mn solute). Most significantly, the existence of a local minimum in the diffusion energy barrier is accompanied with the occurrence of the maximum in the magnetic moment across the 3d row. We find that Mn has the largest magnetic moment among the 3d solute atoms: the magnetic moments (evaluated within the Goldschmidt radii) are $-0.4\mu_B$, $-1.2\mu_B$, $3.1\mu_B$, $2.7\mu_B$, and $1.7\mu_B$ for V, Cr, Mn, Fe, and Co solutes, respectively (the negative sign here indicates that the moment is coupled antiparallel to the nearest neighbor Ni moment). Obviously, magnetism plays a central role in determining the diffusion energy barrier.

From Cr to Mn, there is a change in the magnetic coupling between the solutes and neighboring Ni atoms, indicating an abrupt change in the d-bonding characteristics. In Mn, the majority-spin d states are nearly fully occupied and do not participate actively in the chemical bonding; on the other hand, the minority-spin d states are less than half filled and the occupied states do not have appreciable ⟨110⟩ directional d-bonding components. Thus, the Mn solute is easy to compress, resulting in a low diffusion energy barrier. In Fe, the minority-spin d states with the directional bonding characteristic become progressively occupied, which accounts for the increase in the diffusion barrier energy from Mn to Fe.

Since the variation in the diffusion energy barrier is largely determined by the characteristics of the d-states occupancy in the electronic structure of solute atoms, we suggest that a similar diffusion trend can be expected in other types of metallic host lattices. Indeed, our preliminary result for the diffusion of 5d solutes in the open body-centered-cubic Fe shows exactly the same diffusion trend as in the close-packed fcc Ni — a result that further proves our conclusion.

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