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Diffusion of Adatoms on Face-centered Cubic Transition Metal
Surfaces

by

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Diffusion of adatoms on face-centered cubic transition metal surfaces

Leslie Suzanne Perkins

**Major Professor: Andrew E. DePristo
Iowa State University**

The mechanisms and associated energetics for adatom diffusion on the (100) and (110) surfaces of Ni, Cu, Rh, Pd, and Ag are investigated in this dissertation. Self-diffusion studies have been performed on the (100) and (110) surfaces of Ni, Cu, Pd and Ag using the corrected effective medium method (CEM) and the approximation to CEM used for molecular dynamics and Monte Carlo studies (MD/MC-CEM). Self-diffusion on Pd(100), Ag(100), Ni(110), Cu(110), Pd(110), and Ag(110) is accomplished by the classical view of diffusion: the adatom hops from its equilibrium adsorption site over an intervening bridge site to an adjacent equilibrium site. Self-diffusion on Ni(100) and Cu(100) proceeds by atomic-exchange diffusion mechanism: the adatom on the surface displaces an atom in the first surface layer. This is found only when the explicit calculation of the electronic kinetic-exchange-correlation term is included in the determination of the energy.

Aside from the explicit inclusion of the kinetic-exchange-correlation energy, it is critical to include enough movable atoms in the calculation to insure the correct energetics. The distortions induced by these diffusion mechanisms, especially atomic

exchange, are long ranged in the surface plane. This is due to the fact that small distortions of many atoms is energetically favored over large distortions of few atoms.

The energetics and rates of heterogeneous adatom diffusion on the (100) surfaces of Ni, Cu, Rh, Pd, and Ag are presented. It is found that the final state energies differ due to the variation of metallic bonding with coordination for the different types of metal atoms. This variation with coordination is reflected in the surface energies of the two metals, and thus this macroscopic quantity can be used to correlate the amount of energy gained or released when the adatom displaces a surface atom. This difference in energetic stability of final configurations is also found to generally determine whether bridge hopping diffusion or atomic displacement is the dominant kinetic process in these heterogeneous systems.

DEDICATION

I would like to dedicate this dissertation to my mother, without whom I would not have had the stamina, the courage, and the spirit to have completed this bold undertaking.

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GENERAL INTRODUCTION

Dissertation Organization

Papers written about doctoral research in the format required for each journal are included in this dissertation. *Self-diffusion mechanisms for adatoms on FCC(100) surfaces*, includes an initial study of the energetics of homogeneous adatom diffusion on the (100) surfaces of Ni, Cu, Pd, and Ag. This paper has been published in Surface Science. A study of the energetics and rates of homogeneous adatom diffusion on the (110) surfaces of these same metals is included in *Self-diffusion of adatoms on FCC(110) surfaces*. The paper, *Heterogeneous adatom diffusion on fcc(100) surfaces: Ni, Cu, Rh, Pd, and Ag*, is a study of energetics and rates of diffusion for the twenty heterogeneous adsorbate-substrate combinations of Ni, Cu, Rh, Pd, and Ag. *The influence of lattice distortion on atomic self-diffusion on fcc(001) surfaces: Ni, Cu, Pd, Ag*, is an examination of the effect of the number of active atoms in the system on the energetics of diffusion. The last three papers have been submitted for publication in Surface Science.

Literature Review

The migration of atoms across well-defined single crystal surfaces is a basic event in surface science. A fundamental understanding of many surface phenomena, such as epitaxial thin film growth, nucleation and heterogeneous catalysis, requires knowledge of the behavior of atoms on solid surfaces. This understanding becomes

more important as scientists and engineers attempt to control the growth of solids at the atomic level. In the area of nanostructures, one finds that quantum structures are formed by the control of the placement of atoms [1]. A stunning example of this is the quantum "corrals" that have been created using scanning tunneling microscopy (STM) to arrange Fe atoms on Cu(111) [2]. In the quantum corrals, the Fe atoms are arranged in a circle, and the STM images show a rippled density of states inside the circle of Fe atoms. These results closely match the solutions of the Schrödinger equation for a particle-in-a-box. To achieve such control, it is essential to obtain a fundamental understanding of how an atom interacts with a surface.

Surface diffusion has been used as a microscopic probe into the interactions between adsorbates and surfaces since its discovery by Volmer and Estermann in 1921 [3]. The activation energies associated with the migration of an adatom or cluster on a surface allow one to estimate the strength of the interaction between adsorbate and substrate, as well as determine the topography of the surface. It has been found on W(110) and W(112) that the activation barriers of adatom diffusion for the 5d series of atoms Ta, W, Re, Ir, and Pt [4,5] depend upon the adsorption energies of the adatom with the surface in question. Comparing the activation barriers of the adatoms on the two substrates, it was found that the activation energy for the diffusion of an adatom decreases with decreasing corrugation of the substrate.

Field ion microscopy (FIM) is the primary experimental tool for studying surface diffusion, due to its capacity to resolve individual atoms. For extensive reviews on FIM studies of surface diffusion, the reader is referred to ref. [6,7]. FIM is able to resolve

single atoms on the tip surface. However, the surfaces used in FIM studies are only 20-100 Angstroms in size, so that there are effects due to plane boundaries. Assuming that the diffusion constant on these surfaces follows an Arrhenius form, a plot of the logarithm of the mean square displacement over time versus the inverse of the temperature yields both the activation energy of diffusion and the prefactor to diffusion. The displacement distributions obtained using FIM give information about the geometrical aspects of the diffusion and how they are related to the substrate. The accuracy of the activation barriers and the prefactors is determined by the range of temperatures at which the FIM data are accrued.

It is worthwhile to mention an intrinsic limitation in FIM. In order to achieve resolution of the surface, large electric fields must be applied. Therefore, only metals with a large cohesive energy can be studied with FIM.

Another experimental method that can resolve individual atoms and has been used to study surface diffusion is STM [8]. The surface area that can be analyzed with STM is much larger (approximately 100-10 000 Angstroms) and of a wider variety than those studied with FIM. However, STM is not able to resolve single atoms, due to the mobility of single atoms at the temperatures at which STM measurements are conducted. Other experimental methods employed to study surface diffusion have included low energy electron diffraction (LEED), and thermal energy atom scattering (TEAS). The area considered by these techniques is very large and only macroscopic information can be obtained directly with these methods.

The classical view of diffusion is that an adatom, initially bound in an

equilibrium adsorption site on the surface, migrates to an adjacent equilibrium adsorption site by hopping over an intervening bridge site. This first half of this mechanism is shown in Figure 1 below. This bridge-hopping mechanism has been identified via FIM for a variety of systems: Rh/Rh(100) [9], Ni/Ni(110) [10], Pd/Pt(001) [11], and Pt/Rh(100) [12]. Bridge hopping of adatoms has also been seen for self-diffusion on the (111) surfaces of Rh [9], Ni [10], and Ir [13].

There is another type of diffusion mechanism that was discovered for adatom diffusion on fcc(110) surfaces by FIM. In 1978, Bassett and Webber [14] found that the diffusion of Pt and Ir adatoms occurred in two dimensions on Pt(011) and Ir(011). The imaged adatom began in one the 2-fold adsorption site in one channel of the surface. After an imaging interval, the adatom appeared in an adjacent channel on the surface. This two dimensional diffusion mode was confirmed by Wrigley and Ehrlich [15] for the diffusion of Ir and W atoms on Ir(110). Wrigley and Ehrlich were the first to report that this two dimensional diffusion occurred via an exchange mechanism: the adatom displaces an atom from the (110) channel wall, allowing the adatom to incorporate into

the surface and the surface atom to occupy an adsorption site on the surface. This two dimensional diffusion has been found in the self-diffusion on Ni(110) [10] and the diffusion of a Pt adatom on Ni(110) [16].

The atomic exchange diffusion mechanism has also been found for adatom diffusion on fcc(100) surfaces. After the discovery of this type of mechanism on the Al(100) surface using self-consistent field - local density (SCF-LD) calculations by Feibelman [17], FIM experiments were performed to find other examples of atomic exchange on fcc(100) surfaces. FIM studies have shown that atomic replacement occurs for self-diffusion on the Pt(001) [18] and Ir(001) [19] systems and for the heterogeneous systems Ni/Pt(001) [18b] and Pt/Ni(001) [20]. For an extensive overview of experimental data, it is suggested that the reader consult ref. [21]. A depiction of the atomic exchange diffusion mechanism on fcc(100) surface is shown below.

Theoretical studies of surface diffusion have been ongoing. One theoretical method to obtain activation energies, prefactors, and diffusion constants is a molecular dynamics (MD) simulation. MD involves the propagation of the classical equations of

motion in time for the atoms in a given simulation. Many of the initial MD studies of surface diffusion used the pairwise additive Lennard-Jones (12-6) potential to describe the substrate-substrate and the adsorbate-substrate interactions for the motion of adatoms and clusters on fcc(100), fcc(110), and fcc(111) surfaces [22-24]. In these studies, qualitative agreement was found with various experimental studies, especially by De Lorenzi and coworkers [24], who found that MD with the Lennard-Jones(12-6) potential described the atomic displacement mechanism on a fcc(110) surface. Other MD studies of surface diffusion have used an effective medium based theory to describe the interaction between atoms [25,26]. The effective medium theory, and specifically the corrected effective medium theory (CEM) will be discussed in a later section. Since the time step of MD studies is 10^{-14} second, the order of the vibrational frequency of an atom, it is computationally intractable to model diffusion that occurs on the time scale of microseconds.

To overcome this limitation of MD, another commonly used method to study surface diffusion, and implemented in the papers included in this dissertation, is transition state theory (TST) [27-29]. TST is a method that is used to calculate reaction rates from reactant state to product state. TST can be applied here since surface diffusion is an activated process. The interatomic potential between the adsorbate atom and the substrate is generally corrugated with a variety of adsorption sites that are separated by potential energy (activation) barriers. These barriers are in general large compared to thermal energies.

There are two assumptions made about the reaction dynamics in TST: (1) Once

the transition state is achieved, the reaction proceeds irreversibly from reactant to product, and (2) an equilibrium exists between the reactant and the transition states. This allows one to use equilibrium statistical mechanics to determine the reaction rate.

The TST rate constant is given by the following equation,

$$k_{TST} = v_o e^{-\frac{E_{act}}{k_B T}} \quad (1)$$

where

$$v_o = \frac{\prod_{i=1}^{3N} v_i}{\prod_{i=1}^{3N-1} v_i^{\ddagger}} \quad (2)$$

The activation energy E_{act} is the difference in the energies between the initial and transition states. The TST prefactor, given in Equation 2, assumes that the degrees of freedom are wholly vibrational in the study of surface diffusion, since the crystal does not translate or rotate. These vibrational frequencies are considered to be harmonic, and the classical partition function is used for these low frequencies [30].

There have been theoretical surface diffusion studies that have implemented TST using effective-medium based theories. Effective Medium (EM) studies by Hansen and coworkers on Cu/Cu(001) [31] have found that the replacement mechanism is favored if an explicit correction for changes in the 1-electron energy spectrum is included in the theory. Hansen, et al. have found that channel diffusion of a Cu adatom on Cu(110) has

a lower activation barrier than that for cross-channel diffusion [28]. Embedded Atom Method (EAM) calculations performed by Liu, et al. [31] have corroborated the experimental evidence that Pt migrates on Pt(001) surfaces via an atomic exchange mechanism. In this same study, Liu and coworkers found that the replacement mechanism is favored for self diffusion on Au(001) and Pd(001), while bridge hopping is energetically preferred for self-diffusion on Ni(100), Cu(100), Ag(100) and the (110) surfaces of Ni, Cu, Pd, Ag, Pt, and Au. Corrected Effective Medium (CEM) calculations presented in this dissertation have found that atomic exchange is favored for self-diffusion on Ni(100), Cu(100), and Cu(110). The bridge hopping diffusion mechanism is energetically favored for self diffusion on Ag(100), Pd(100) and the (110) surfaces of Ni, Pd, and Ag. The qualitative disagreement between the EAM and CEM methods is discussed in the fourth paper included in this dissertation.

Corrected Effective Medium Theory

This basic effective medium theory relies on an approach to chemical bonding which is based upon replacing the N-atom system with N individual atom embedded in homogeneous electron gas systems [35].

Complete details of the CEM method are contained in refs. [36-41] to which the interested reader is referred. Here, we present only that information needed to comprehend the application of the method to surface processes.

For a set of N-atoms, $\{A_i, i=1, \dots, N\}$, the CEM theory utilizes the following equations to calculate the interaction energy:

$$\Delta E(\{A_i\}) = \sum_{i=1}^N \Delta E_{EXLM}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V_c(i, j) + \Delta G(\{A_i\}) \quad (3)$$

$$n_i = \frac{1}{2Z_i} \sum_{i,j=1}^N \int n(A_i; \mathbf{r}-\mathbf{R}_i) n(A_j; \mathbf{r}-\mathbf{R}_j) d\mathbf{r} \quad (4)$$

$n(\mathbf{r}-\mathbf{R}_i)$ is the unpolarized atomic electron density distribution (from Hartree-Fock calculations) while Z_i and $\mathbf{R}_i$ are the atomic number and nuclear position, respectively. This equation is valid under the assumption that the total system electron density can be approximated as the superposition of atomic electron densities:

$$n(\mathbf{r}) = \sum_i n(A_i; \mathbf{r}-\mathbf{R}_i) \quad (5)$$

The first term in Equation (3) is the sum of the embedding energy for each atom, each term of which is solely a function of the average electron density environment of that particular type of atom. The subscript EXLM indicates that these functions are provided by forcing the CEM method to duplicate: (1) the results of self-consistent linearized muffin tin orbital density functional calculations [42] on the cohesive energy of the homogeneous bulk solid at lattice constants from 30% expansion to 10% contraction [39]; (2) the experimental diatomic binding curve [36] from equilibrium to 5% expansions. For surface diffusion, low coordination bonding can occur and thus we have utilized the EXLM functions for all of the calculations. In addition, $V_c(i,j)$ is the sum of the electron-electron, electron-nuclear, and nuclear-nuclear

coulombic interactions between atoms A_i and A_j . ΔG is an explicit correction for the kinetic-exchange-correlation energy difference between the inhomogeneous electron density in the real N-atom system and the many effective atom-jellium systems.

Since the kinetic-exchange-correlation energy is so intensive numerically, a simple approximation to the CEM method has been developed and used in a number of molecular dynamics (MD) and Monte-Carlo (MC) simulations of large systems [25,26]. This MD/MC-CEM formula replaces Equation (3) with

$$\Delta E(\{A_i\}) = \sum_{i=1}^N \Delta F_{EXLM}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N V_c(i, j) \quad (6)$$

The ΔF_{EXLM} are the new "effective" embedding energy functions, which are also determined by forcing the MD/MC-CEM method to agree with the same data as did the CEM method.

The potential energy is determined by specifying the chemical identities of all atoms in the system. This determines the electron densities [43] which then allows for computation of the $V_c(i,j)$, $\Delta G(\{A_i\})$ and the density overlaps.

SELF-DIFFUSION MECHANISMS FOR ADATOMS ON FCC(100) SURFACES

A paper published in *Surface Science*

Leslie S Perkins and Andrew E. DePristo

Abstract

We investigate the mechanisms and associated energetics of diffusion for the Ni/Ni(100), Cu/Cu(100), Pd/Pd(100) and Ag/Ag(100) systems using the corrected effective medium method. The Ni/Ni(100) and Cu/Cu(100) systems are shown to favor the atomic-exchange diffusion mechanism whereas the Pd/Pd(100) and Ag/Ag(100) systems favor the bridge-hopping diffusion mechanism. The explicit inclusion of the kinetic-exchange-correlation energy is critical to determination of the favored mechanism. A simple model, based upon binding "curves" from dimer and bulk binding, is developed to provide a physical explanation of the different behavior exhibited by the various metal systems.

1. Introduction

Diffusion of adatoms on metal surfaces is integral to important surface processes such as heterogeneous catalysis and epitaxial thin film growth. The primary experimental tool for studying surface diffusion is field ion microscopy (FIM), due to its capacity to resolve individual atoms. Metals adatoms which have been studied are W [1,2], Pt [3-9], Ir [2,7,9-19], Ni [3,20-22], Cu [23] and Rh [2,24] on a variety of substrates.

On the (100) face of an fcc metal (which is the focus of the present article), two diffusion mechanisms have been observed experimentally: (1) the adatom hops from a 4-fold hollow site to an adjacent 4-fold hollow site over the intervening 2-fold bridge site (i.e. bridge-hopping mechanism); and, (2) the adatom replaces an atom in the first substrate layer which then moves to the 4-fold hollow site diagonal from the adatom's original 4-fold site (i.e. replacement or exchange diffusion mechanism). In addition, another possible high symmetry diffusion path involves the adatom hopping over a substrate atom to occupy a 4-fold site diagonal from its original position (i.e. atop-hopping mechanism). Perspectives of the first half of these three diffusion mechanisms can be found in Figure 1. (The final half is not shown because the reader can construct it by symmetry.)

FIM studies have shown that atomic replacement is preferred for the homogeneous Pt/Pt(001) [5-7] and Ir/Ir(001) [14] systems and the heterogeneous Ni/Pt(001) [6] and Pt/Ni(001) [9] systems, while bridge-hopping is preferred for the

Pd/Pt(001) [6] system. Self-consistent field local-density (SCF-LD) functional calculations have shown that Al/Al(001) [25] is energetically favored to diffuse via a replacement mechanism. Embedded Atom Method (EAM) studies [26] have found that the replacement mechanism is favored for the Au/Au(001), Pd/Pd(001) and Pt/Pt(001) systems. Effective Medium (EM) studies on Cu/Cu(001) [27] have found that the replacement mechanism is favored if an explicit correction for changes in the 1-electron energy spectrum is included in the theory.

It is worthwhile to discuss the SCF-LD results [25] since these predicted the favoring of the replacement mechanism before any experimental data was available and also since these provide some insight into the electronic structure changes. The driving force for the replacement mechanism was found to be the formation and dissolution of covalent bonds between the Al adatom in the replacement transition state and the Al adatom in the equilibrium initial state. The Al adatom thus changed from covalent bonding with four nearest neighbor surface atoms to covalent bonding with three surface atoms. In other words, two effects occurred: the change in bond strength with coordination and the formation of stronger directional covalent bonds, involving sp-hybrid orbitals. Such bonds may require non-spherical electron densities to be described properly.

In this paper, we present our results on the mechanisms for homogeneous diffusion on the (100) faces of Ni, Pd, Cu, and Ag, using the corrected effective medium (CEM) theory [28-33] to generate the interaction energies and forces. The CEM method (as well as the related EAM and EM theories) utilizes spherical electron densities in its

present implementation[‡] and thus cannot be expected to treat the strong directional bonding in the Al/Al(100) system. The method does describe the variation of bond strength with coordination (as tested for diatomic molecules [29,33], metal clusters [28b,32] and surface energies [30,31]) which should be the most important for the Ni, Cu, Pd and Ag systems with nearly filled d-shells and weak directional bonding. All three of the proposed diffusion mechanisms have been studied and the results are presented in this paper.

2. Method

2.1. CEM theory

Complete details of the CEM method are contained in refs. (28-34) to which the reader is referred. Here, we present only that information needed to comprehend the application of the method to surface processes.

For a set of N-atoms, $\{A_i, i=1, \dots, N\}$, the CEM theory utilizes the following equations to calculate the interaction energy:

[‡]The CEM method has utilized non-spherical and spin-polarized electron densities in the treatment of bonding in the NO-Ag(111) system [34] but these electron densities did not change with orientation or separation of the NO from the Ag(111). Thus, it is more precise to state that the CEM method does not allow for self-consistent changes in directional electron densities, which is what would be needed to treat the Al/Al(100) replacement diffusion process.

$$\Delta E(A_i) = \sum_{i=1}^N \Delta E_{\text{EXLM}}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V_c(i,j) + \Delta G(A_i) \quad (1)$$

$$n_i = \frac{1}{2Z_i} \sum_{j=1}^N \int n(A_i; r-R_j) n(A_j; r-R_j) dr \quad (2)$$

$n(r-R_j)$ is the unpolarized atomic electron density distribution (from Hartree-Fock calculations) while Z_i and R_i are the atomic number and nuclear position, respectively. This equation is valid under the assumption that the total system electron density can be approximated as the superposition of atomic electron densities:

$$n(r) = \sum_i n(A_i; r-R_i) \quad (3)$$

The first term in Eq. (1) is the sum of the embedding energy for each atom, *each term of which is solely a function of the average electron density environment of that particular type of atom.* The subscript 'EXLM' indicates that these functions are provided by forcing the CEM method to duplicate: (1) the results of self-consistent Linearized Muffin Tin Orbital density functional calculations [35] on the cohesive energy of the homogeneous bulk solid at lattice constants from 30% expansion to 10% contraction [31]; (2) the experimental diatomic binding curve [36] from equilibrium to 5% expansions. Smoothly joining these regions [33] then defines $\Delta E_{\text{EXLM}}(A_i; n_i)$ for each type of atom A_i . In addition, $V_c(i,j)$ is the sum of the electron-electron, electron-nuclear, and nuclear-nuclear coulombic interactions between atoms A_i and A_j . ΔG is an explicit

correction for the kinetic-exchange-correlation energy difference between the inhomogeneous electron density in the real N-atom system and the many effective atom-jellium systems.

Since the kinetic-exchange-correlation energy is so intensive numerically, a simple approximation to the CEM method has been developed and used in a number of molecular dynamics (MD) and Monte-Carlo (MC) simulations of large systems [37].

This MD/MC-CEM formula replaces Eq.(1) with

$$\Delta E(\{A_i\}) = \sum_{i=1}^N \Delta F_{EXLM}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N V_c(i,j) \quad (4)$$

The ΔF_{EXLM} are the new "effective" embedding energy functions, which are also determined by forcing the MD/MC-CEM method to agree with the same data as did the CEM method.

We emphasize that the potential energy is determined by specifying the chemical identities of all atoms in the system. This determines the electron densities [38] which then allows for computation of the $V_c(i,j)$, $\Delta G(\{A_i\})$ and the density overlaps. The only flexibility pertains to the choice of embedding function which may or may not utilize the diatomic bonding region. In the latter case, these are referred to by the subscript 'LMTO'. Both the 'EXLM' and 'LMTO' embedding functions contain detailed information on the variation of twelve-fold bonding with distance. The 'EXLM' embedding curves also provide information on variation of bonding at very low coordination and are thus more complete. For surface diffusion, low coordination

bonding can occur and thus we have utilized the 'EXLM' functions throughout this paper. These embedding functions are shown for Ni, Cu, Pd and Ag in Figure 2. The "effective" embedding functions are shown for the same atoms in Figure 3. It is worthwhile to emphasize that the scale in these figures is very large compared to diffusion barriers so although the general shape of ΔE_{EXLM} and ΔF_{EXLM} are similar, one should not expect that the diffusion energetics will be similar, especially since the ΔG term may vary differently for surfaces than for bulk systems.

2.2. Computational Method

Calculations on the (100) surface were performed using 4 layers of atoms, 6 unit cells on a side in the first and third layers and 5 unit cells on a side in the second and fourth layers, for a total of 170 atoms. There are thirteen movable (or active) atoms, nine in the first layer and four in the second layer. The active zone is arranged to be symmetric about the center active atom in the first substrate layer. The energies of the initial and final geometries for each of the diffusion mechanisms were minimized with respect to the positions of the adatom and the active surface atoms using a quasi-Newton minimization scheme of the Broyden family[39]. This was a 42-dimensional minimization. These minimized configurations were then used as the initial and final states for the determination of the minimum energy path (MEP). We used the algorithm developed by Ulitsky and Elber [40] for the calculation of steepest descent paths. The initial guess in the MEP evaluation was a straight line which connects the two minima

and along which were identified 10 equally spaced grid points in the 42-dimensional space. A new point was added near the saddle point between the two minima after each minimization cycle in order to closely bracket the transition state [32]. The first MEP evaluations were performed with the MD/MC-CEM method since this was very fast computationally. This optimized MEP determined using the MD/MC-CEM theory was used as the first guess in the calculation of the MEP using the CEM method.

3. Results

The general results of the detailed CEM and MD/MC-CEM calculations are summarized in Table 1. Activation energies are defined as $E_a = \Delta E(\text{transition state}) - \Delta E(\text{initial state})$ and similarly for the kinetic-exchange-correlation energy contribution, $\Delta G_a = \Delta G(\text{transition state}) - \Delta G(\text{initial state})$.

First, focus on the CEM results which indicate that the replacement mechanism is slightly favored over the bridge-hopping mechanism for Ni/Ni(100) and Cu/Cu(100). The bridge-hopping mechanism is strongly favored for the Pd/Pd(100) and Ag/Ag(100) systems. Second, note that the MD/MC-CEM predicted barriers are in reasonable agreement with the CEM ones for the bridge- and atop-hopping barriers (i.e. within ~ 0.15 eV) but are much too large for the replacement mechanism (i.e. errors of ~ 0.75 eV).

Before discussing each system in more detail, we want to emphasize and detail a fundamental theoretical point: the inaccuracy of the MD/MC-CEM values for the replacement mechanism demonstrates that the low coordination, inhomogeneous electron density configuration formed in the replacement transition state is not well described without inclusion of the kinetic-exchange-correlation term (ΔG). It is apparent from Table 1 that the contribution of ΔG favors the replacement over bridge mechanisms by 0.34 eV on Ni and 0.10 eV on Cu. This is larger than the difference in activation energies for these mechanisms, and thus the favored mechanism would be reversed without the explicit contribution of ΔG . For Pd/Pd(100) and Ag/Ag(100), ΔG is not much different for either the bridge or replacement mechanisms and thus bridge hopping is favored.

For Cu, the above effect in the CEM formalism agrees totally with the previous EM work by Hansen, Stoltze, Jacobsen, and Nørskov [27] in which the explicit addition of the one-electron correction term led to a favoring of the replacement over the bridge-hopping diffusion for the Cu/Cu(100) system. The 1-electron correction term is very similar in the EM theory to the ΔG term in the CEM theory. To be more quantitative, the bridge and replacement barriers without 1-electron corrections are estimated from the figure in ref.[27] as 0.35 eV and 1.12 eV, respectively, which are in good agreement with the MD/MC-CEM values that do not include ΔG . Inclusion of the 1-electron corrections in the EM method yields 0.41 eV and 0.23 eV, respectively, again taken from the figure in ref.[27]. Given the difference between the two methods for including explicit corrections, the agreement between CEM and EM must be considered very good.

Experimentally, the Cu/Cu(100) system has been studied with He atom scattering by de Miguel et al. [41] and Ernst, Fabre, and Lapujoulade [42]. The former estimated $E_a=0.48$ eV from an Arrhenius plot of the surface diffusion coefficient data obtained from the values of stationary intensities of the He atom scattering peaks at temperatures ranging from 220 K to 420 K. The latter estimated $E_a=0.28 \pm 0.06$ eV from data over a temperature range from approximately 100 K to 250 K, with Arrhenius behavior exhibited between 160 K and 250 K. The CEM values are in much better agreement with the 0.48 eV value, but a definitive comparison must await further experimental measurements.**

Now, consider the Ni/Ni(100) system. The study by Tung and Graham [22] used an assumed "normal" pre-exponential frequency of $\nu=10^{13}$ Hz and an average jump length of 2.5 Å in the simplified transition state formula $D=\nu\langle l^2 \rangle \exp(-E_a/kT)$ to yield $E_a=0.63$ eV from their measured value of $D=10^{-17}$ cm² s⁻¹ at the onset $T=225$ K. This value is in excellent agreement with the CEM result for both the bridge-hopping and the atomic-replacement diffusion barriers.

An interesting experimental consequence may occur based upon the CEM predictions of the small difference in energy between the activation barriers for the replacement and bridge-hopping mechanisms in both the Ni and Cu systems. With two

** A private communication from Professor J. Evans notes that the He atom scattering experiment determines the product of a critical growth exponent and a diffusion barrier, with the former depending upon the critical nucleation size. If the former is varied slightly, one can easily get large changes in E_a and this could influence the results of Ernst et al.

different hopping rates, the site visitation map of an adatom may not be uniform (and may be thought of as a superposition of $c(2 \times 2)$ and $p(1 \times 1)$ patterns, at least as a first approximation). At present, this detailed diffusion information is unavailable since the desorption field of these adatoms on the (100) surface is lower than the normal Ne best image field. Thus, at the fields which the adatoms desorb, the substrate is not distinctly imaged and therefore does not allow for mapping of the sites visited by the adatom. However, advances in computer image analysis and video recording systems may make it feasible to obtain a site-visitation map for the diffusion of a Ni adatom on Ni(100), providing that the adatom does not desorb at the imaging field. Therefore, experimental verification of our results that Ni diffuses on Ni(100) via both bridge hopping and atomic-exchange mechanisms should be possible.

Now, we attempt to provide further insight into the physical driving force behind the results of Table 1. To do so, we first consider a few atom-atom distances for the geometries at the bridge and replacement transition states as summarized in Table 2. It is immediately apparent that the replacement transition state has three nearly equal distances: 1/ between the adatom and the atom it replaces, and 2/ between the adatom and two nearest surface atoms (at the corners of the initial unit cell). And these distances are contracted about 11% for every metal. By contrast, the bridge transition state has two equal distances to the nearest surface atoms but this distance displays much more variation with metal. The second nearest neighbor atoms in the bridge transition state are very far away.

Next we performed a full geometrical analysis of the entire set of active atoms. The distances between the fourteen active atoms (adatom included) and all other atoms were calculated for the initial and transition states. These "bond lengths", were placed in a histogram with a limit of 20% expansion to 20% contraction of R_{NN} (the bulk nearest neighbor distance). Results for the four-fold hollow, bridge transition state and replacement transition state for Ni and Pd may be found in Figure 4. The favoring of the exchange over the bridge-hopping mechanism can be qualitatively associated with the number and degree of contracted bonds in the exchange transition state.

To understand this in a more quantitative way, it is helpful to note bond energies (eV) and distances (bohr) for the dimer [36] and the bulk [43] as listed in table 3, and as duplicated exactly by the CEM theory (using ΔE_{EXLM}). These data illustrate that the variation of bond strength with distance and coordination varies considerably among these metals. Such variation can be used to understand behaviors evident in Table 1 by the following simple model.

As a first approximation, we simply included the coordination dependence of the metal-metal bond strength by dividing the bond energy among the neighbors [44] and then let the variation of bond length determine the bond energy. This is the simplest physically reasonable bond energy versus bond length method. The curves constructed from the dimer and the bulk for each metal are shown in Figures 5 and 6. The energy of each metal-metal bond is then calculated from the simple linear relationship: where R_0 is the distance at which $E_{bond}(R_0)=0$.

$$E_{bond}(R) = -\frac{E_{coh}}{12} + \left(\frac{E_{coh}}{12} - \frac{D_e}{2}\right) \frac{(R - R_{NN})}{(R_e - R_{NN})} \quad R < R_o \quad (5)$$

$$R_o = R_{NN} + \frac{(R_{NN} - R_e)}{\frac{6D_e}{E_{coh}} - 1} \quad (6)$$

Using this equation, energies were calculated for each of the geometries of each metal using the values displayed in Figure 4 for Ni and Pd. Activation barriers for the replacement diffusion relative to the hopping diffusing barrier are -0.9 eV, -2.0 eV, +0.2 eV and +1.2 eV for Ni, Cu, Pd and Ag, respectively. It is not surprising that the numbers are not in good agreement with the full CEM calculation but the favoring of the mechanism is right in every case. Thus, the variation in bond energy with coordination and distance provides a qualitative explanation of the present full CEM calculations.

The model can also be useful in analyzing experimental data and making simple predictions of diffusion mechanisms. For example, examining Figure 5, one notes that the bonding curve of Pt lies substantially below that of Ni which in turn lies somewhat below that of Pd. Thus, we would predict that Pt strongly favors the replacement diffusion mechanism, which has been found previously to be true experimentally [5-7]. Furthermore, applying the same reasoning to Figure 6, we predict that Au should also favor the replacement diffusion mechanism over the bridge-hopping mechanism, since the Au bonding "curve" lies below that of the Cu bonding curve.

Finally, we consider the results of the approximation to CEM, MD/MC-CEM, in more detail. The numbers in Table 1 show that the bridge-hopping mechanism is the most energetically-favored path for diffusion for all of the (100) faces studied. As noted previously, the data on Cu/Cu(100) is in agreement with the EM results of Hansen, et al. [27] for which no 1-electron term was used. This is extremely important because it indicates that neglect of the kinetic-exchange-correlation energy term can lead to significant errors even in two very different formulations.

An empirical theory which uses the concept of atoms embedded in jellium is the EAM. In this case, one constructs both empirical two body and embedding functions. There is no inclusion of any kinetic-exchange-correlation energy term. In Table 4, we reproduce the MD/MC-CEM values from Table 1 as well as the EAM Voter-Chen (EAM-VC) activation barriers from ref.[26]. The MD/MC-CEM and EAM-VC 'effective' embedding functions are comparable since both include information about the diatomic binding and bulk cohesive energy curves. The EAM values [26] for the surface energy are significantly smaller than the MD/MC-CEM values [31] and the experimental results on polycrystalline samples[45]. This indicates that the bond strengths of the 6-9 fold coordinated atoms are too large in the EAM. The results in table 3 follow from this observation. E_a for the bridge-hopping process are in good agreement for Ni, Pd, Cu, and Ag, indicating that the very low electron density regime is described similarly by both methods, as it should since they both utilize the diatomic molecule to get this region of the embedding curves. However, the energies for the atomic replacement

mechanism are smaller by 0.3-0.7 eV in the EAM, a direct consequence of overestimating the bond strength in the medium coordination regime.

4. Conclusions

The central theoretical conclusion of this paper is that the explicit inclusion of kinetic-exchange-correlation energy terms is critical to a proper description of the binding in the replacement transition state, and thus to any prediction of the competition between hopping and replacement diffusion mechanisms. This amplifies and extends to a number of systems the finding by Hansen, et. al. [27] for Cu/Cu(100) that the barrier for hopping and replacement diffusion could only be predicted correctly by EM theory upon addition of a term to account for the difference between the one-electron spectrum in the system under study and in the bulk fcc crystal.

An interesting experimental consequence of the present results follows from the prediction that differences between the activation barriers of the replacement and bridge-hopping mechanisms for Cu and Ni are on the order of 0.05 eV. Therefore, one would expect both mechanisms to be present with different rates at different temperatures. This could be probed by determining the site visitation map for the adatom.

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Table 1: Calculated activation barriers, E_a (eV), for diffusion on fcc(100) surfaces along with the contribution of the kinetic-exchange-correlation energy term, ΔG_a

	CEM		MD/MC-CEM
	E_a	ΔG_a	E_a
Ni			
Bridge	0.68	0.00	0.62
Replacement	0.65	-0.34	1.40
Atop	1.15	-0.12	1.03
Cu			
Bridge	0.47	-0.24	0.52
Replacement	0.43	-0.34	1.10
Atop	0.72	-0.38	0.89
Pd			
Bridge	0.64	-0.28	0.75
Replacement	1.03	-0.31	1.38
Atop	1.11	-0.52	1.30
Ag			
Bridge	0.41	-0.43	0.45
Replacement	0.58	-0.41	1.01
Atop	0.66	-0.48	0.74

Table 2: CEM calculated geometries in the transition state for the bridge and replacement mechanisms. Distances are expressed as the fraction of the bulk nearest-neighbor distance, R_{NN} . $R_{t,1-2}$ is the distance between the diffusing adatom and the surface layer atom undergoing replacement while $R_{x,i}$ is the distance between the diffusing adatom and one of its i^{th} nearest-neighbors in the surface plane, where x is "b" or "r". The subscripts "b" and "r" distinguish bridge and replacement transition states.

atom	$R_{b,1}/R_{NN}$	$R_{b,2}/R_{NN}$	$R_{t,1-2}/R_{NN}$	$R_{t,1}/R_{NN}$
Ni	0.87	1.30	0.88	0.88
Cu	0.92	1.33	0.88	0.89
Pd	0.89	1.30	0.89	0.89
Ag	0.94	1.37	0.88	0.90

Table 3: Bond energies (eV) and distances (bohr) for the dimer [36] and the bulk [43]

atom	Diatomic		Bulk		D_e/E_{coh}	R_e/R_{NN}
	D_e	R_e	E_{coh}	R_{NN}		
Ni	2.092	4.16	4.44	4.70	0.47	0.885
Cu	2.046	4.20	3.49	4.82	0.59	0.871
Pd	1.040	5.01	3.99	5.20	0.27	0.963
Ag	1.672	4.70	2.95	5.46	0.57	0.861
Pt	3.730	4.42	5.84	5.24	0.64	0.844
Au	2.300	4.67	3.81	5.45	0.60	0.857

Table 4: Calculated activation barriers, E_a (eV)

	MD/MC-CEM	EAM-VC ^a
Ni		
Bridge	0.62	0.68
Replacement	1.40	1.15
Cu		
Bridge	0.52	0.53
Replacement	1.10	0.79
Pd		
Bridge	0.75	0.74
Replacement	1.38	0.59
Ag		
Bridge	0.45	0.48
Replacement	1.01	0.60

^a Reference [23]

Figure 1. View of the diffusion mechanisms on the (100) surface from initial state to transition state: (a) bridge-hopping; (b) atop hopping; (c) atomic exchange

Figure 2. The embedding curves, ΔE_{EXLM} , for Ni, Pd, Cu, and Ag

Figure 3. The "effective" embedding functions, ΔF_{EXLM} , for Ni, Pd, Cu, and Ag

Figure 4a. Histograms of the distances between atoms in the four-fold initial state geometries for Ni and Pd

Figure 4b. Histograms of the distances between atoms in the bridge-hopping transition state geometries for Ni and Pd

Figure 4c. Histograms of the distances between the atoms in the atomic-replacement transition state geometries for Ni and Pd

Figure 5. Bonding curves from bulk and dimer data for Ni, Pd, and Pt

Figure 6. Bonding curves from bulk and dimer data for Cu, Ag, and Au

SELF-DIFFUSION OF ADATOMS ON FCC(110) SURFACES

A paper submitted to *Surface Science*

Leslie S. Perkins and Andrew E. DePristo

Abstract

We investigate the mechanisms and associated energies of diffusion for the Ni/Ni(110), Cu/Cu(110), Pd/Pd(110) and Ag/Ag(110) systems using the corrected effective medium (CEM) method. On the (110) surface, cross-channel diffusion can occur via atomic exchange of the adsorbate atom with an atom of the channel wall or by hopping over the short-bridge site located in the channel wall. We find that the barrier for cross-channel diffusion is much smaller for the atomic exchange path. In-channel diffusion occurs via hopping over the long-bridge site. We find that the activation barrier associated with in-channel diffusion is smaller than the activation barrier associated with cross-channel diffusion by 0.17, 0.01, 0.03 and 0.08 eV for Ni, Cu, Pd and Ag, respectively. We also investigate convergence of the activation barriers by varying the number of active atoms in the simulations. Decreases of 0.3-0.6 eV are found as the number of active atoms is increased from nearest neighbors to a (converged) large number of active atoms; this is due to relaxation of the strain. The decreases are nearly identical for the in-channel and cross-channel mechanisms.

Introduction

Catalysis and film growth depend upon mass transport via diffusion of atoms and molecules on solid surfaces. The primary experimental tool for studying surface diffusion is field ion microscopy (FIM), due to its ability to resolve individual atoms. Diffusion of metals adatoms on Pt [1], Ni [2-5], Ir [6-8], Cu [9] and Rh [10] FCC(110) surfaces have been studied. On the (110) surface, diffusion occurs via three mechanisms: cross-channel via atomic exchange of the adsorbate atom with an atom of the channel wall; cross-channel via hopping over the short-bridge site located in the channel wall; in-channel via hopping over the long-bridge site.

Experimental studies have shown that cross-channel diffusion by atomic exchange is preferred for Ir on the unreconstructed Ir(110) surface [8], Pt on Pt(110) [1] and Pt on Ni(110) [5]. FIM data has also shown that there are both cross-channel and in-channel diffusions for Ni on Ni(110) [3]. Embedded atom method (EAM) calculations [11] have found that self-diffusion via hopping over the long-bridge site is energetically preferred for Al, Ni, Cu, Pd, Ag, Pt and Au. An effective medium (EM) study on Cu(110) [12] has shown that in-channel diffusion has a lower activation barrier than that for cross-channel diffusion.

In this paper, we present energies for self-diffusion on the (110) face of Ni, Cu, Pd and Ag. In-channel diffusion over the long-bridge site and cross-channel diffusion via atomic exchange are considered because preliminary calculations indicated that the cross-channel hopping mechanism has a much higher activation barrier. The corrected

effective medium (CEM) method [13-18], a non-self-consistent electron density functional theory, is used to generate the interaction energies and forces. This method describes the variation of bond strength with coordination and distance, a property that should be dominant for the Ni, Cu, Pd and Ag systems with nearly filled d-shells. This variation has been tested for diatomic molecules [14,18], metal clusters [13b,17,18] and surface energies [15,16].

Since CEM calculations are still expensive computationally, we also present results using the much faster and simpler modification with the acronym, MD/MC-CEM. For both the theories we also explore a fundamental computational issue, namely the effect of the number of atoms on the calculated energies of diffusion.

Method

Complete details of the CEM and MD/MC-CEM theories are contained in refs. [13-18] with a brief summary of the aspects relevant to diffusion calculations found in ref. [19]. Thus, we present only the particular information needed for self-diffusion on the FCC(110) surface.

Calculations on the (110) surface were performed using a system with 4 layers of atoms, 9 unit cells x 7 unit cells in layers one and three and 8 x 6 in layers two and four, for a total of 222 atoms. A top view of the (110) surface used for these calculations appears in figure 1. Two sets of calculations were performed, differing only

in the number of movable (i.e., active) surface atoms: 1) 9 active atoms in the first layer and 4 in the second layer for a total of 13 active surface atoms; 2) 25 active atoms in the first layer and 16 in the second layer for a total of 41 active surface atoms. The active zone was arranged in both cases to be symmetric about the center atom in the first substrate layer.

The energies of the initial and final geometries for each of the diffusion mechanisms were minimized in a $3N$ -dimensional coordinate space, where N is the number of active atoms. This minimization was performed using the method of deepest descent. These minimum energy configurations were then used as the initial and final states for the determination of the minimum energy path (MEP). We used the algorithm developed by Ulitsky and Elber [20] for the calculation of steepest descent paths. All MEP calculations were initiated using the MD/MC-CEM theory with the initial guess for the MEP being a straight line (in $3N$ dimensions) connecting the two 2-fold adsorption minima. Ten equally spaced grid points were placed along this straight line. A new point was added near the saddle point between the two minima after each minimization cycle to closely bracket the transition state [17] yielding a final total of 29 points along the MEP. The optimized MEP, determined using the MD/MC-CEM theory, was used as a first guess in the much slower CEM calculations in order to obtain faster convergence.

Results and Discussion

Table 1 contains the calculated activation barriers for the two mechanisms using 42 active atoms.⁶ Examining the activation barriers obtained using CEM, we find that in-channel hopping is energetically favored for self-diffusion in each of the systems studied.

The initial study of self-diffusion on the Ni(110) surface was performed by Tung and Graham [3] using FIM. The sample was prepared by thermal annealing. At temperatures from 145 K to 195 K, the tip was imaged in 60 second intervals. Activation barriers to diffusion were obtained from the Arrhenius equation of diffusion, $D = D_0 \exp(-E_a/kT)$, leading to values of 0.23 ± 0.04 eV and 0.32 ± 0.05 eV for in-channel and cross-channel diffusion, respectively. These activation energies are in good agreement with the long-bridge hopping and atomic exchange barriers found in Table 1.

However, the prefactors, D_0 , reported by Tung and Graham were 10^{-9} cm²/s and 10^{-7} cm²/s for the in-channel and cross-channel mechanisms, respectively. Indeed, we have calculated prefactors to diffusion using the MD/MC-CEM theory, finding 3.93×10^{-3} cm²/s and 1.32×10^{-2} cm²/s for in-channel and cross-channel diffusion, respectively. These deviate greatly from Tung and Graham's values and the expected prefactors to diffusion on (110) surfaces, such as those reported for Pt and Rh [3] which have ranged between 10^{-3} and 10^{-1} cm²/s. Tung and Graham's experimental data has been reanalyzed

⁶ In a few calculations of cross channel diffusion via hopping over the short-bridge site, we found very high diffusion barriers. Thus, this mechanism is not reported here.

[4,11] recently using standard prefactors of $1 \times 10^{-3} \text{ cm}^2/\text{s}$ for both mechanisms. The recalculated activation barriers were found to be 0.45 eV for both processes. These new activation barriers differ greatly from those calculated by both CEM and MD/MC-CEM methods in table I.

The reanalysis is not without problems though. If one were to draw a "best-fit" line for all of the data points for diffusion on the thermally annealed Ni(110) surface in figure 7 of ref. [3], one can calculate an average activation barrier for self-diffusion on the Ni(110) surface from the slope of the line. This yields an average activation barrier of 0.28 eV. This does not agree with the recalculated value mentioned above (0.45 eV) which appears to lie outside the error bars reported by Tung and Graham.

It appears that Tung and Graham's original analysis and the recent reanalysis leads to results which are not entirely consistent. As such, we believe that it is necessary to perform further FIM experiments and perhaps full SCF-DF calculations to resolve these problems.

To the best of our knowledge, there are no experimental studies of self-diffusion on Cu(110). However, the (110) surface was included in a study of self-diffusion on Cu surfaces by Hansen et. al. [12]. Using the EM theory with explicit 1-electron corrections, Hansen, et al. have found that self-diffusion on Cu(110) has the lowest activation barrier for in-channel hopping. We estimate from the figure in ref. [12] that the in-channel and cross-channel (exchange) barriers are 0.18 eV and 0.26 eV, respectively. By contrast, the CEM results in Table 1 indicate essentially equal barriers for both mechanisms. It is not apparent which method is more accurate, and thus this

system is also a candidate for SCF-DF calculations.

Returning to the general trends in Table 1, we consider the activation barriers obtained from the MD/MC-CEM approximation to CEM. The MD/MC-CEM values follow the same trends as those from the CEM method, but the in-channel hopping is always favored more in MD/MC-CEM than in CEM. The differences in activation barriers between the two methods are within 0.05 eV for the long-bridge barriers of Ag(110) and Pd(110) and the atomic exchange barrier of Ag(110).

Table 2 contains the MD/MC-CEM activation barriers as well as activation barriers obtained by Liu, et. al. [11] using the EAM method as parametrized by Voter and Chen (EAM-VC). We find the agreement between the MD/MC-CEM and EAM-VC numbers to be reasonable, especially for the Pd and Ag systems.

The final point that we considered is the convergence of the diffusion activation barriers with the number of active atoms. This is treated in greater detail in another paper [21] but we present the results for FCC(110) surfaces here. Activation barriers are listed for two sets of CEM and MD/MC-CEM calculations performed for each self-diffusion system in Table 3. The first column of data corresponds to 13 active atoms in the first two substrate layers. The second column of data corresponds to 41 active atoms in the first two substrate layers. A sharp change is seen between the two sets of activation barriers. The smallest difference is 0.25 eV for the Pd long-bridge hop whereas the largest difference is 0.58 eV for the Cu long-bridge hop. The drastic change in activation barriers can be understood based upon the fact that there is considerable perturbation of the surface for both in-channel and cross-channel diffusions.

When only 13 atoms in the surface are allowed to respond to the movement of the adsorbed atom, this perturbation of the lattice is confined to a small area, and each atom must shift a great deal to accommodate this. However, distributing this perturbation among 41 surface atoms reduces the shift of each surface atom. This same behavior has been seen in surface diffusion calculations using EAM [22].

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Table 1. **Activation barriers (in eV) for self-diffusion on (110) surfaces as calculated using CEM and MD/MC-CEM theories. These values correspond to a total of 223 atoms, with 41 moving surface atoms in the first 2 layers of the surface and 1 moving adsorbate atom.**

		CEM	MD/MC-CEM
Ni			
	Bridge	0.18	0.24
	Replacement	0.35	0.41
Cu			
	Bridge	0.08	0.26
	Replacement	0.09	0.49
Pd			
	Bridge	0.30	0.28
	Replacement	0.33	0.42
Ag			
	Bridge	0.26	0.25
	Replacement	0.34	0.36

Table 2. Activation barriers for self-diffusion on (110) surfaces. Also included are EAM (Voter-Chen parametrized) activation barriers reported by Liu, et al. in reference [11].

		MD/MC-CEM	EAM-VC
Ni			
	Long Bridge	0.24	0.39
	Replacement	0.41	0.42
Cu			
	Long Bridge	0.26	0.26
	Replacement	0.49	0.49
Pd			
	Long Bridge	0.28	0.30
	Replacement	0.42	0.34
Ag			
	Long Bridge	0.25	0.25
	Replacement	0.36	0.31

Table 3. CEM activation barriers calculated using two active zones. The first has 9 and 4 atoms in the top two layers while the second has 25 and 16 in the top two layers.

		13 active	42 active
Ni	Long Bridge	0.60	0.18
	Replacement	0.75	0.35
Cu	Long Bridge	0.66	0.08
	Replacement	0.61	0.09
Pd	Long Bridge	0.55	0.30
	Replacement	0.61	0.33
Ag	Long Bridge	0.73	0.26
	Replacement	0.80	0.34

Figure 1. Top view of the (110) surface.

HETEROGENEOUS ADATOM DIFFUSION ON FCC(100) SURFACES: Ni, Cu, Rh, Pd, Ag

A paper submitted to Surface Science

Leslie S. Perkins and Andrew E. DePristo

Abstract

We present activation barriers and prefactors for the migration of heterogeneous adatoms on fcc(100) surfaces. Two mechanisms are considered in this paper: 1) hopping of the adatom from one four-fold hollow site to an adjacent four-fold hollow site via a two-fold bridge site; and 2) exchange of the adatom with an atom in the first surface layer. Twenty heterogeneous combinations of Ni, Cu, Rh, Pd, and Ag were treated using transition state theory, and select comparisons were made to the results of finite temperature molecular dynamics simulations. The interaction potentials were generated using the Molecular Dynamics/Monte Carlo Corrected Effective Medium (MD/MC-CEM) theory throughout. We find that the final state energies differ due to the variation of metallic bonding with coordination for the different types of metal atoms. This variation with coordination is reflected in the surface energies of the two metals, and thus this macroscopic quantity can be used to correlate the amount of energy gained or released when the adatom displaces a surface atom. Due to the non-directional character

of metallic bonding in the fcc metals, this difference in energetic stability of final configurations is also found to generally determine whether bridge hopping diffusion or atomic displacement is the dominant kinetic process in these heterogeneous systems.

Introduction

For a homogeneous adatom/fcc(100) metal substrate combination, two diffusion mechanisms have been observed experimentally with field ion microscopy (FIM): (1) the adatom hops from a 4-fold hollow site to an adjacent 4-fold hollow site over the 2-fold bridge site between the two sites (i.e., bridge hopping mechanism); and, (2) the adatom replaces an atom in the first substrate layer, which then moves to the 4-fold hollow site diagonal from the adatom's original 4-fold site (i.e., atomic exchange mechanism). For a heterogeneous adatom/substrate combination, the situation is more complex. Hopping over the bridge site is still considered diffusion. However, atomic displacement by exchange may be the initial stage of nearly irreversible alloying if the adatom is more stable as an impurity atom in the surface than as an adsorbate atom on the surface.

FIM studies of heterogeneous systems have been primarily concerned with the substrates of W [1-7], Pt [8-10], Ir [11-14], and Ni [15]. However, there have been few studies of heterogeneous diffusion on fcc(100) surfaces. Kellogg found that a Ni adatom displaces a surface atom of Pt(100) while a Pd adatom hops over the bridge on Pt(100) [9]. Tsong and Chen found that a Re adatom displaces a surface atom of Ir(100) [14].

Kellogg also determined that a Pt adatom displaces a surface atom of Ni(100) and Ni(110) [15] while a Pt adatom hops over the bridge on Rh(100) [16].

In this paper, we present results of transition state theory (TST) calculations on the heterogeneous atomic displacement of Rh, Ni, Pd, Cu, and Ag adatoms on the (100) surfaces of these metals. The data reported are the activation energies and prefactors for the bridge hopping and atomic exchange mechanisms.

Method

We have employed the molecular dynamics/Monte Carlo corrected effective medium method (MD/MC-CEM) to describe the interaction potentials in our calculations. Complete details of the MD/MC-CEM theory are contained in refs. [17-20] with a brief summary of the aspects relevant to diffusion calculations found in ref. [17]. The calculations on the (100) surfaces were performed using a total of 5 layers of atoms, 13 atoms on a side in the first, third and fifth layers, and 12 atoms on a side in the second and fourth layers (Fig. 1). This substrate size was chosen since it yields activation barriers converged to within 0.01 eV [21]. Of the 795 atoms in the substrate, there are 226 movable (active) atoms located in the first three layers, 81 active atoms in the first and third layers and 64 active atoms in the second layer. The active atoms were arranged to be symmetric about the center active atom in the first substrate layer.

The energies of the initial and final geometries for each mechanism were minimized in 3N-dimensional coordinate space, where N is the number of active atoms,

using the method of deepest descent. The minimized configurations were then used as the initial and final states for the determination of the minimum energy path (MEP), as described in a previous paper [17].

We have used transition state theory (TST) to calculate the rates of bridge hopping and atomic exchange in each heterogeneous system. TST is one of the simplest methods used to calculate the rates between the initial and final binding sites and has been previously employed in the study of surface diffusion [22, 23]. Details of these expressions may be found in ref. [22], to which the interested reader is referred.

The TST rate equation is given by

$$k_{TST} = v_o e^{-\frac{E_{act}}{k_B T}} \quad (1)$$

where

$$v_o = \frac{\prod_{i=1}^{3N} v_i}{\prod_{i=1}^{3N-1} v_i^{\ddagger}} \quad (2)$$

The activation energy, E_{act} , is the difference in energy between the transition state and the reactant state, and v_o is the TST prefactor. We have assumed that the degrees of freedom are wholly vibrational since the crystal does not translate or rotate, and that

these are harmonic. Furthermore, the classical partition function was used because these are low frequencies.

Results and Discussion

We begin by studying the energetics of the stable reactant and product configurations. The adsorption energies for these two configurations play an important role in understanding the kinetics of diffusion and exchange in these systems. The first configuration is the adatom adsorbed in a four-fold hollow equilibrium site. This is the initial and final state for the bridge hopping mechanism, and the initial state for the exchange mechanism. The second is the adatom adsorbed in the surface of the substrate with one substrate atom adsorbed in the nearest four-fold equilibrium site. This is the final state for the exchange mechanism.

The values for the adsorption energies, labeled by "four-fold" and "impurity" for the adsorbed and substrate locations, respectively, are presented in table 3. The difference in the two values can be understood most simply in terms of the (100) surface energies of the metals [19], which are 1.30, 1.05, 0.95, 0.78 and 0.58 eV/atom for Rh, Ni, Pd, Cu and Ag, respectively. The surface energy is roughly the energy required to change a 12-coordinated bulk atom into an 8-coordinated surface atom. This loss of coordination reduces the binding energy, and such a reduction continues through even lower coordinations [24]. As such all atoms favor higher coordination binding sites.

The atom with higher surface energy will gain more energy moving to an impurity location (8-coordinated) from a four-fold hollow location (5-coordinated) than the atom with lower surface energy will lose in the reverse process. Thus, the atom with higher surface energy will be more stable in the impurity location after displacing the original substrate atom. All results in table 1 follow this rule except two.

The two unusual values in table 1 involve Pd and Ni: Pd favors an impurity location in Ni(100) while Ni favors a four-fold hollow location on Pd(100). To understand these exceptions, one must look in more detail at the variation in the atomic interaction energy, $E_i(A)$, with coordination "i". The difference in energy between the impurity and four-fold hollow locations is just $E_8(\text{substrate}) + E_8(\text{adsorbate}) - E_5(\text{adsorbate}) - E_5(\text{substrate})$. Following ref.(24) which found a straight line variation of $E_i(A)$ with "i" from the dimer ($i=1$) to the bulk ($i=12$), one expresses this energy difference as $(-3/11)\{[E_{12}(\text{substrate}) - E_1(\text{substrate})] - [E_{12}(\text{adsorbate}) - E_1(\text{adsorbate})]\}$. The values of $E_{12} - E_1$ are -4.3, -3.39, -3.37, -2.47 and -2.12 eV for Ni, Pd, Cu and Ag, respectively. The values for Ni and Pd are so close because the Ni dimer interaction energy is -2.1 eV while that of Pd is -1.04 eV. With such a small difference in impurity v.s. four-fold hollow sites, the favoring of the Pd impurity in Ni(100) can be determined by variations of interaction energy with distance, which can only be predicted via detailed calculations not such a simple binding energy model. Note also that the Cu/Ag(100) and Ag/Cu(100) systems almost disobey the surface energy rule because of the large size difference which increases the importance of the variation of interaction energy with distance. For

the other systems, however, we emphasize that the surface energy variation is sufficient to understand the trends.

Next we study the energetics of the transition states, i.e., the activation barriers resulting from the detailed MD/MC-CEM MEP calculations. These are reported for each heterogeneous adatom-substrate combination in table 2 for both the bridge hopping mechanism, $E_{act}(\text{bridge})$, and the exchange mechanism, $E_{act}(\text{exchange})$.

The bridge hopping mechanism results are easily understood in terms of the adatom changing from 5-coordinated to 2-coordinated bonding. Using the same simple model as above yields $E_{act}(\text{bridge}) = (-3/11)[E_{12}(\text{adsorbate}) - E_1(\text{adsorbate})]$. This expression is independent of substrate and, from the above mentioned data, one finds 1.17, 0.92, 0.92, 0.67 and 0.58 eV for Rh, Ni, Pd, Cu and Ag, respectively. As expected since there is no relaxation allowed in this model, the values overestimate the exact numbers in table 2. However, all the trends are correct, including the similarity of Pd and Ni and that of Ag and Cu.

The exchange mechanism is much more complex since the transition state can involve a variety of coordinations depending upon the separations between the adatom and the substrate atom which it replaces. And, since both adatom and substrate change coordination, the barrier varies substantially with substrate (in contrast to the hopping barrier). Nevertheless, some sense can be made of the numbers in table 2 based upon the lack of strong angular bonding in fcc metals. If the final state of the exchange is lower in energy than that of the hopping mechanism, the exchange is preferred, and one might expect that the exchange barrier would be lower than the hopping barrier. This is

true for eight of the ten cases with the exceptions being Rh/Ni(100) and Pd/Ni(100). For the former, this exception is surprising since the impurity is favored by 0.55 eV in table 1. The increased size of Rh relative to Ni makes the exchange barrier larger (i.e., one is forcing a large Rh atom into a small Ni hole).

For the Pd/Ni(100) system, exchange is only slightly favored in table 1 and the Pd is much larger than the Ni, thereby making the barrier to exchange larger. The Pd/Ni(100) and Ni/Pd(100) systems are interesting because the exchange process is less favorable than the hopping process by kinetics in both cases even though the impurity is favored in the former by energetics.

Table 3 contains the pre-exponential factors, ν_0 , for the bridge hopping and atomic exchange mechanisms. All the values fall within the expected range of 10^{12} to 10^{13} Hz characteristic of localized vibrations in metallic systems. It is difficult to make any general analysis of these values because of the strong coupling between the adatom and the substrate even for the bridge hopping process. For example, we show the variation of the prefactor as a function of the number of active atoms in Fig. 2. The values change considerably from the limiting case of just the moving adatom to that of moving a large number of substrate atoms also. The use of a rigid substrate to estimate the prefactors is obviously only good as a very rough approximation for metal on metal substrates [23].

To see more details, we present the vibrational density of states for only a moving adsorbate and for 227 active substrate and adsorbate atoms in Fig. 3. One can easily see that the adsorbate frequencies are embedded in the lattice vibrational state

distribution. This means that the adsorbate motion will strongly couple to lattice motion. Indeed, we have found that the lattice is severely distorted by the moving adatom. As such, note that the prefactors vary substantially with substrate identity for the same type of adatom. This contradicts the behavior found in ref. [23] which indicated that the prefactor mainly depended upon the identity of the adatom. The difference is of course that ref. [23] used a rigid substrate which did not allow for coupling of the adatom and substrate motion while the present study treats such coupling accurately by allowing a large number of substrate atoms to respond.

From the prefactors and the activation energies, we can calculate the rates for both the bridge-hopping and atomic exchange mechanisms from Eq.(1) provided that we also incorporate the fact that there are four equivalent paths for both process. This yields

$$k = 4 \nu_0 e^{(-E_{act}/k_B T)}. \quad (3)$$

For the Rh/Ag(100) system, there have been molecular dynamics simulations of atomic exchange from both gas phase deposition and various surface coverages [25, 26]. In deposition studies, the adsorption energy facilitates the exchange of a heterogeneous adatom with an atom in the substrate [25]. Therefore, the rates obtained from the present TST calculations would be an underestimate of the data obtained from dynamics calculations using a constant deposition process [26]. Furthermore, high coverages of Rh were found to facilitate the exchange process via cooperative displacement [25].

Thus, the isolated atom rates in Eq.(3) can only be compared to the MD simulations at very low coverages.

We use the results of MD simulations for an initial $p(6 \times 6)$ coverage of Rh on Ag(100) at substrate temperatures of 300 and 400 K [26]. These found that after 50 ps, 2% of the Rh atoms displaced surface Ag atoms at 300 K and 31% displaced Ag atoms at 400 K. For first order kinetics, the fraction of atoms that have exchanged, n_{exch} , after a time "t" is

$$n_{\text{exch}} = 1 - e^{-kt} . \quad (4)$$

Using Eqs. (3) and (4) and the data in tables 2 and 3, we find the TST predictions to be 3% and 30%, respectively, in excellent accord with the MD simulations.

Displacements of Ag(100) surface atoms by Rh adatoms has been found experimentally by Schmitz, et al. [27]. To make a detailed comparison to their data, one must determine many more kinetic rates especially for two and three atom Rh clusters, and for the case when the surface already has a fraction of Rh atoms. The good agreement with the MD simulations at low coverage here indicates that such an approach may be worthwhile.

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Table 1: Adsorption energies (in eV) for a heterogeneous adatom in the four-fold equilibrium site (upper value) and for the heterogeneous atom impurity in the (100) surface with the substrate metal atom in the four-fold equilibrium site (lower value).

substrate : adatom→	Rh	Ni	Pd	Cu	Ag
↓					
Rh					
four-fold		-3.68	-3.25	-3.15	-2.66
impurity		-3.20	-2.75	-2.32	-2.61
Ni					
four-fold	-4.18		-3.08	-2.99	-2.89
impurity	-4.73		-3.17	-2.62	-2.34
Pd					
four-fold	-3.93	-3.32		-2.88	-2.67
impurity	-4.36	-3.26		-2.53	-2.08
Cu					
four-fold	-3.81	-3.14	-2.77		-2.66
impurity	-4.62	-3.44	-3.24		-2.61
Ag					
four-fold	-3.29	-2.85	-2.28	-2.54	
impurity	-4.06	-3.15	-2.75	-2.55	

Table 2: The activation barriers (in eV) computed from MD/MC-CEM calculations. The first barrier corresponds to the adatom (element reported in the top row) diffusing via a bridge hopping mechanism on the corresponding substrate (element listed in the left column). The second barrier corresponds to the same adatom exchanging with an atom in the substrate layer.

substrate : adatom→	Rh	Ni	Pd	Cu	Ag
↓					
Rh					
bridge		0.75	0.73	0.53	0.51
exchange		1.21	1.46	1.44	1.91
Ni					
bridge	0.65		0.64	0.45	0.44
exchange	0.85		1.10	1.23	1.47
Pd					
bridge	0.75	0.70		0.52	0.50
exchange	0.70	0.78		0.98	1.34
Cu					
bridge	0.72	0.64	0.73		0.48
exchange	0.42	0.57	0.59		0.91
Ag					
bridge	0.73	0.70	0.76	0.55	
exchange	0.26	0.33	0.38	0.52	

Table 3: Prefactors (in 10^{12} Hz) in Eq.(2) for the bridge hopping (upper value) and atomic exchange (lower number) processes.

substrate : adatom→	Rh	Ni	Pd	Cu	Ag
↓					
Rh					
bridge exchange		5.82 6.50	4.07 8.64	2.46 3.62	3.31 4.14
Ni					
bridge exchange	8.28 9.37		9.77 11.93	4.15 3.76	7.80 4.45
Pd					
bridge exchange	7.85 13.76	7.01 9.74		2.63 3.98	4.96 6.38
Cu					
bridge exchange	12.43 10.61	9.44 9.00	17.57 15.58		9.07 7.50
Ag					
bridge exchange	9.69 3.43	18.24 7.29	16.08 4.01	34.02 14.44

Figure 1: Top view of the (100) surface used in these studies.

Figure 2: Prefactor of the transition theory rate constant calculated from Eq. (2) as a function of the number of active substrate plus adatom.

Figure 3: Vibrational density of states for the initial four-fold equilibrium adsorption site and the bridge hopping transition state. These are shown for only an active adatom in "a" and "b" and for an active adatom plus 226 active substrate atoms in "c" and "d".

THE INFLUENCE OF LATTICE DISTORTION ON ATOMIC SELF-DIFFUSION ON FCC(001) SURFACES: Ni, Cu, Pd, Ag

A paper submitted to *Surface Science*

Leslie S. Perkins and Andrew E. DePristo

Abstract

We present the variation of the activation barriers with the number of movable substrate atoms for the self-migration of adatoms on fcc(001) surfaces. Two mechanisms considered in this paper are: 1) hopping of the adatom from one four-fold hollow site to an adjacent four-fold hollow site via a two-fold bridge site; and 2) exchange of the adatom with an atom in the first surface layer. While both mechanisms distort the lattice atoms from their ideal positions, the latter process is found to lead to much greater distortions than the former. We find at least a 25% reduction in the barrier to atomic exchange as the number of substrate atoms is increased from a minimum to very large. This is shown to be due to sharing of the lattice distortion over many substrate atoms, thereby reducing the distortion of each atom significantly. Nevertheless, the explicit inclusion of the kinetic-exchange-correlation electronic energy terms in the interactions is still found to be critical in predicting the energetically favored self-diffusion mechanism on the fcc(001) surface.

Introduction

There have been a number of theoretical papers in recent years that have focussed on the energetics of self-diffusion of adatoms on the simple cubic faces of fcc transition metals [1-7]. The theoretical methods used in these studies employed effective medium theory, an approach to chemical bonding based upon replacing the N-atom system with N individual atoms embedded in homogeneous electron gas systems [8]. The different implementations have led to considerable variation among the results presented in these papers, especially in the identification of the energetically-favored diffusion mechanism for self-diffusion on fcc(001) surfaces. In each of these papers, there have been two diffusion mechanisms studied: (1) the adatom hops from an equilibrium adsorption site to an adjacent equilibrium adsorption site over an intervening 2-fold bridge site (i.e., bridge-hopping mechanism); and, (2) the adatom replaces an atom in the first substrate layer which (i.e., atomic exchange mechanism).

Hansen and coworkers [2] have found using the effective medium theory (EM) that a Cu adatom energetically favors migration by atomic exchange on Cu(001). This was corroborated qualitatively in calculations using the corrected-effective medium theory (CEM) [5]. In ref. [5], we also found that self-diffusion on Ni(001) energetically favors atomic exchange while that on the Pd(001) and Ag(001) favors bridge hopping. However, Liu, et al. [3] using the embedded atom method (EAM) determined that self-diffusion on Cu(001) and Ni(001) energetically prefers bridge hopping while self-diffusion on Pd(001) favors atomic exchange.

In a recent paper by Cohen and Voter [8], the convergence of various surface diffusion barriers was shown to be very sensitive to the number of active layers used in the calculations. This fact in conjunction with the inconsistencies between the above methods for the energetically preferred mechanisms of diffusion and also for the values of the two activation barriers have prompted us to reexamine our calculations on (001) surfaces of Ni, Cu, Pd, and Ag. In particular, we have investigated the effect of the number of active atoms on the diffusion barriers associated with bridge hopping and atomic exchange. This enables a critical comparison of the results obtained from the different effective medium theories.

In accord with our previous results, we find qualitative agreement with the EM results of Hansen et al. [2]. We believe this is due to the inclusion of an explicit correction for changes in the 1-electron energy spectrum in the EM theory, a term analogous to the explicit calculation of kinetic-exchange-correlation energy differences in the CEM theory. By contrast, since the EAM does not explicitly calculate an energy correction term to account for inhomogeneities in the electronic density, the CEM results do not agree even qualitatively with those from EAM. The MD/MC-CEM values and the EAM do agree rather well, lending further support to the importance of the explicit correction term.

Finally, we also indicate how simple theories that are adequate for describing lattice inhomogeneity could be used in conjunction with sophisticated theories of chemical bonding to provide accurate diffusion barriers using even a small numbers of active atoms.

Method

To test the convergence of our activation barriers, calculations were performed using nine unique active zones as listed in table 1. Each layer contains a square region of movable atoms and each cluster contains a number of such layers. Start with the active zone containing 13 atoms and used by us previously [5]. It is shown in Fig. 1a having 13 active atoms in the first 2 layers, with 3 atoms on a side in the first layer and 2 atoms on a side in the second layer. For convenience, we utilize the shorthand notation (3,2) for 3-by-3 and 2-by-2 in the first and second layers, respectively. The next active zone, denoted by (5,4), is shown in Fig. 1b. The next two active zones added further active layers, (5,4,5) and (5,4,5,4). A larger three-layer active zone, (7,6,7) is shown in Fig. 1c. The two largest active zones greatly increased the number of movable atoms in these three layers to (9,8,9) and (11,10,11) as shown in Figs. 1d and 1e, respectively. Finally, the special cases of a rigid surface, (0), and one active substrate atom, (1) are included in table 1 since these are the smallest possible values for bridge hopping and exchange diffusion, respectively.

Each active zone was surrounded by fixed atoms in plane and by entirely fixed layers underneath to ensure that the small cluster retained the shape of the (001) surface. The total size of the cluster is described in the same notation as for the size of the active zone. The particular sizes used for each calculation are also shown in Fig. 1 and listed in table 1.

We have employed the molecular dynamics/Monte Carlo corrected effective medium method (MD/MC-CEM) and the corrected effective medium method with explicit electron kinetic-exchange-correlation correction term (CEM) to calculate the interactions for each nuclear geometry. Complete details of the CEM and MD/MC-CEM theory are contained in refs. [9-13] with a brief summary of the aspects relevant to diffusion calculations found in ref. [5]. The determination of the activation barrier was done by calculating the minimum energy path (MEP). The MEP was found using the algorithm developed by Ulitsky and Elber [14] for the calculation of steepest descent paths, with specific details as in a previous paper [5].

Results

We present detailed results for self-diffusion in the Pd(001) system in order to illustrate the general features due to lattice distortion. Other systems will then be shown to exhibit the same characteristics.

In table 1, we present the MD/MC-CEM activation barriers for self-diffusion on Pd(001) using the nine different active zones. An activation barrier is considered converged when the variation with increasing active zone is less than 0.01 eV. For bridge hopping diffusion, the activation energy decreases by only 0.015 eV from 13 to 41 active atoms and by less than 0.001 eV afterwards. Thus, convergence is attained for 41 active substrate atoms in 2 layers.

Note that adding more active atoms in each layer or adding more layers does not alter the value of the bridge hopping barrier to even 0.001 eV after 134 active substrate atoms are included. This indicates that migration of an adatom from one four-fold hollow adsorption site to an adjacent four-fold hollow site does not greatly perturb the underlying substrate in self-diffusion, since very few atoms are needed to respond to attain a converged value. Indeed, the hopping exchange diffusion barrier decreases only 0.1 eV from the rigid surface result, about 12%.

However, perturbation of the substrate is very important for the exchange of an adatom with an atom from the first surface layer. The activation energy decreases by 0.47 eV upon increasing the number of active substrate atoms from the minimum of 1 to 13, by another 0.26 eV from 13 active atoms in 2 layers to 41 active atoms in 2 layers, and by another 0.06 eV until convergence is attained at 226 active atoms in three layers. From the data in table 1, we conclude that adding the third layer of atoms for a total 66 active substrate atoms further reduces the barrier by 0.04 eV from the 41 active atom case. An additional layer of atoms does not significantly reduce the activation energy. From these comparisons, we believe that the distortions induced by the adatom penetrating the first surface layer can be effectively described using three active layers.

The lateral distortions in the substrate caused by atomic exchange are not as short-ranged. Keeping 3 active layers, we compare the activation energies with respect to increasing the number of atoms present in each active layer, $(n,m,n) \rightarrow (n+2,m+2,n+2)$ for $n=5,7,9$ and $m=n-1$. Comparing the atomic exchange barriers of the 66 and 134 active atom calculations, there is a decrease of about 0.09 eV. Adding more atoms to

each active layer, for a total of 226 active substrate atoms, further decreases the activation energy by approximately 0.03 eV. The atomic exchange activation energy is converged at 226 active substrate atoms as the 343 active atom result is within the convergence limit.

The differences in the atomic exchange activation energies with respect to the size of the active zone support the assertion that the atomic exchange mechanism perturbs the lattice much more than the bridge hopping mechanism. The reduction in the activation barrier is due the fact that as more atoms are allowed to respond to the insertion of the adatom in the first substrate layer, the less each atom must displace to accommodate the adatom, thereby lowering the lattice distortion energy. In the harmonic limit and under the gross approximation of a diagonal and equal element force constant matrix, the lattice distortion energy is proportional to the sum of the square differences in the positions of the active substrate atoms between the initial state configuration and the transition state configuration. This summed square displacement has been calculated for the x-, y-, and z-components of the substrate atoms as shown in Figures 2 and 3 as a function of the number of active substrate atoms for the bridge hopping and atomic exchange mechanisms, respectively.

In Fig. 2, there are significant changes in the average displacements of the bridge hopping diffusion mechanism between 0 active atom and 66 active atoms but much smaller changes after that. The difference in the x-, y-, and z- distortions for the bridge hopping mechanism are simple to understand. When the adatom is hopping over the

bridge, atoms in the substrate plane will be carried along with it in the direction of the motion, namely the x- and z- directions in our path calculation.

In Fig. 3 for the exchange diffusion, there are large changes in the sum of the square z-displacements of the atoms until 226 active atoms are used, at which point convergence of the sum is attained. There are slight increases in the x- and y-displacements as we add more substrate atoms. A feature to notice is that as more active atoms are added in the surface layers, the stress induced in the lattice by atomic exchange is felt in the x- and y- directions, and reduced in the z-direction. The reason for this is that shifting an atom a small amount in the plane of the surface is much more favorable than distorting the surface layers in the z-direction.

Comparing figures 2 and 3, one sees that the adatom moving over the bridge site on the surface disturbs the substrate lattice by approximately an order of magnitude less than the adatom penetrating the first substrate layer since fewer atoms are needed to accommodate the displacement of the adatom. From table 1, we can estimate the lattice distortion energy as the difference between the activation energy with the smallest active zone and that with the converged active zone. This is 0.1 eV for the bridge hopping and 0.9 eV for the exchange barriers, respectively, again roughly an order of magnitude less for the former.

In table 2, we present our previously reported [5] and the present converged MD/MC-CEM activation barriers for self-diffusion on the (001) surfaces of Ni, Cu, Pd, and Ag. There are only minor changes in the bridge hopping barriers as the active zone is increased from 13 to 226 atoms for these systems. There are significant decreases of

0.3 - 0.4 eV for the atomic exchange barriers with the same increase in active zone. Even with the reduction of the latter, the energetically preferred diffusion mechanism using MD/MC-CEM theory is always bridge hopping. This is in complete accord with the conclusions of ref. [5].

In table 2, we also present our previously reported [5] and the present CEM activation barriers using 13 and 134 active atoms, respectively. Unfortunately, there is a limitation in determining the activation barriers using CEM-MEP calculations. The size of the system needed for definitely converged results, 226 active and 795 total atoms, is too large for the memory of the nCUBE 2 hypercube system. On available machines that have enough memory, the calculations are approximately a factor of 25 slower than on the nCUBE 2 system. Because of this, we present the CEM-MEP results in table 2 for 442 total substrate atoms with 134 active substrate atoms. These can be used to obtain an estimate of the converged CEM values by the following procedure.

First, compare the change in the activation barriers from 13 active atoms to 134 active atoms for both MD/MC-CEM and CEM. One finds that the relative change in the atomic exchange barriers between the different number of active atoms is quite comparable for the two methods, with the exception of atomic exchange on Cu(001). This makes physical sense because both CEM and MD/MC-CEM predict very similar lattice distortions and phonon frequencies. Based on this, we estimate the atomic exchange barriers for a CEM MEP calculation using 226 active atoms by linear extrapolation using the same ratio of the relative change in the MD/MC-CEM activation barriers, and applying this to the CEM values. These values are listed in table 2. The

converged values are very similar to those with 134 active atoms, as expected from the MD/MC-CEM results.

The above procedure, using a simpler method to estimate the lattice distortion in conjunction with a more complicated method to determine the energetics of the bonding variation, could also be exploited for full self-consistent density functional theory. Some caution would have to be taken to do this properly since even in the MD/MC-CEM and CEM theories the variation from 13 to 134 atoms is not the same because the atomic geometries differ. Thus, the amount of lattice distortion differs in each, precluding use of a simple constant ratio of the values from the two different theories which would require only one calculation with the more complicated theory. One must use the relative variation that requires at least two calculations with the complicated method and three with the simpler method.

From table 2, we find that the explicit inclusion of the kinetic-exchange-correlation energy is critical in the determination of the favored mechanism. This general feature is also in complete accord with the conclusions of ref. [5]. The converged CEM results show that atomic exchange is strongly preferred (by 0.20-0.26 eV) for self-diffusion on Ni(001) and Cu(001), while in ref. [5] only a weak preference (by 0.03-0.04 eV) was found. Converged values of CEM diffusion barriers in table 2 indicate that competing hopping and bridge diffusion mechanisms would be expected for Ag and, to a lesser degree, Pd. These features correct those mentioned in ref. [5].

With the converged MD/MC-CEM and CEM values at hand, we consider again the comparison to EM, EAM and experimental values as summarized in table 3. For the

Ni/Ni(001) system, a field ion microscope study by Tung and Graham [15] used an assumed "normal" pre-exponential frequency of 10^{13} Hz to yield an activation energy of 0.63 eV from their measured value of $D=10^{-17}$ cm² s⁻¹ at the onset $T=225$ K. This value is too large compared to the CEM exchange barrier on Ni.

For Cu, the converged CEM value is in very good agreement with the previous EM work by Hansen, Stoltze, Jacobsen, and Nørskov [2] with the explicit addition of the one-electron correction term (which is very similar to the explicit kinetic-exchange-correlation term in the CEM theory). In addition, the bridge and replacement barriers without 1-electron corrections are in much better agreement with the MD/MC-CEM values. It is worthwhile to note that the converged atomic exchange activation energy for self-diffusion on Cu(001) is in very good agreement with the value of 0.16 eV as determined from the Evans' and Bartelt's reanalysis [16] of a He-beam diffraction study [17].

For Pd(001), a recent study of the self-diffusion barrier on Pd(001) using LEED [18] has found an activation barrier of 0.61 eV. This is in good agreement with the Pd bridge hopping barrier calculated using CEM in table 3.

Finally, we note that the converged MD/MC-CEM values are in even better agreement with the EAM values than were the unconverged values in ref. [5]. The MD/MC-CEM and EAM (with Voter-Chen parametrization) are comparable since both include information about the diatomic binding and bulk cohesive energy curves. The bridge hopping barriers changed only a little from the values in ref. [5] but the decreases in the atomic replacement barriers have led to very good agreement between MD/MC-

CEM and EAM-VC values, except for Pd(001). For this system, the favored mechanism differs. Further experimental and/or more accurate theoretical calculations are needed to clarify the situation.

Conclusions

We have found that to accurately describe the energetics of adatom diffusion on fcc(001) surfaces, it is necessary that the number of active atoms is sufficient to insure the convergence of the lattice distortion energy. For the bridge hopping mechanism, the distortion is very small and the diffusion barrier converges to within about 0.01 eV with only a few movable substrate atoms. For the atomic exchange process, the distortion is sufficiently large to require at least 3 layers of active atoms, with the active zone extending no less than four nearest neighbors in any direction relative to the central atom in the first surface layer.

In accord with previous work [2,5], we find that explicit inclusion of the kinetic-exchange-correlation energy terms for self-diffusion on the fcc(001) surface is critical in predicting the energetically favored diffusion mechanism. The CEM calculated values of the activation barriers obtained using a large number of active atoms agree well with other theoretical and experimental values.

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Table 1: Cluster sizes and calculated MD/MC-CEM activation barriers (in eV) for bridge hopping and atomic exchange for self-diffusion on Pd(001).

total layers ^a	total # of atoms	active layers ^b	# of active atoms	bridge	exchange
(11,10,11,10)	442	(0)	0	0.824	NA
(11,10,11,10)	442	(1)	1	0.797	1.837
(7,6,7,6)	170	(3,2)	13	0.750	1.370
(11,10,11,10)	442	(5,4)	41	0.735	1.112
(11,10,11,10)	442	(5,4,5)	66	0.728	1.076
(13,12,13,12,13)	795	(5,4,5,4)	82	0.727	1.067
(11,10,11,10)	442	(7,6,7)	134	0.727	0.988
(13,12,13,12,13)	795	(9,8,9)	226	0.727	0.955
(15,14,15,14,15)	1067	(11,10,11)	342	0.727	0.946

- ^a The number of layers is the number of elements in the set while the number of atoms in each layer is n^2 where there are "n" atoms on a side. For example, (7,6,5) has 7^2 atoms in layer 1, 6^2 in layer 2 and 5^2 atoms in layer 3 for a total of 110 atoms. See the text for more details.
- ^b Same as "a" except for only moving atoms.

Table 2: MD/MC-CEM and CEM calculated activation barriers (in eV) for bridge hopping and atomic exchange for self-diffusion on the (001) surfaces of Ni, Cu, Pd, and Ag.

		MD/MC-CEM (# of active atoms)			CEM (# of active atoms)		
		13	134	226	13	134	226 ^a
Ni	bridge	0.62	0.60	0.60	0.68	0.67	0.67
	exchange	1.40	1.03	1.00	0.65	0.49	0.47
Cu	bridge	0.52	0.51	0.51	0.47	0.46	0.46
	exchange	1.10	0.80	0.77	0.43	0.20	0.18
Pd	bridge	0.75	0.73	0.73	0.64	0.64	0.64
	exchange	1.38	0.99	0.96	1.03	0.72	0.70
Ag	bridge	0.45	0.46	0.46	0.41	0.40	0.40
	exchange	1.01	0.73	0.70	0.58	0.43	0.41

^a Estimated from the change in the MD/MC-CEM values.

Table 3: Calculated and experimental activation barriers (in eV) for self-diffusion on the (001) surfaces of Ni, Cu, Pd, and Ag.

	MD/MC- CEM ^a	EAM-VC ^b	EM ^c (w/o 1 electron)	CEM ^a	EM ^d (with 1 electron)	Expt.
Ni						
bridge	0.60	0.68		0.67		
exchange	1.00	1.15		0.47		
						0.63 ^e
Cu						
bridge	0.51	0.53	0.35	0.46	0.41	
exchange	0.77	0.79	1.12	0.18	0.23	
						0.16 ^f
Pd						
bridge	0.73	0.74		0.64		
exchange	0.96	0.59		0.70		
						0.61 ^g
Ag						
bridge	0.46	0.48		0.40		
exchange	0.70	0.60		0.41		

^a Calculated using 226 active atoms. See tables 1 and 2 and the text for more details.

^b EAM values using Voter-Chen parametrization from ref. [3].

^c EM values without explicit 1-electron correction term, as estimated from ref. [2].

^d EM values with explicit 1-electron correction term, as estimated from ref. [2].

^e Field ion microscope data from ref. [15].

^f From the reanalysis in ref. [16] of the He atom scattering data from ref [17].

^g Low energy electron diffraction value from ref. [18].

Figure 1a. Top view of 170 substrate atoms with 13 active atoms in two layers. The active atoms are lighter than the surrounding fixed atoms.

Figure 1b. Top view of 442 substrate atoms with 41 active atoms in two layers. The active atoms are lighter than the surrounding fixed atoms.

Figure 1c. Top view of 442 substrate atoms with 134 active atoms in three layers. The active atoms are lighter than the surrounding fixed atoms.

Figure 1d. Top view of 795 substrate atoms with 226 active atoms in three layers. The active atoms are lighter than the surrounding fixed atoms.

Figure 1e. Top view of 1067 substrate atoms with 342 active atoms in three layers. The active atoms are lighter than the surrounding fixed atoms.

Figure 2. Summed square displacements of the active atoms in the x-, y-, and z-directions for the bridge hopping mechanism on Pd(001). This is shown as a function of the number of active atoms used in the calculation. (The x-direction is $\langle 110 \rangle$, down the rows and the z is $\langle 001 \rangle$, perpendicular to the surface plane.)

Figure 3. Same as Figure 2, except for the atomic exchange self-diffusion mechanism on Pd(001).

GENERAL CONCLUSIONS

This work has focussed on the interaction of adatoms with the simple cubic faces of transition metals. The first and second papers included in this dissertation found that in order to effectively map out atomic motion on a fcc(100) surface, the inclusion of kinetic-exchange-correlation energy correction terms is critical to a proper description of the binding, especially for the atomic exchange diffusion mechanism. The correct description of the diffusion mechanisms is necessary to determine the dominant mechanism for an adatom to migrate across a surface, especially on a fcc(100) surface. In the third paper, it was shown that the interaction between a heterogeneous adatom and a fcc(100) substrate can be related to the surface energies of the respective metals. This type of qualitative information can be useful in determining the likelihood of a sharp interface being epitaxially grown on a surface. The last paper included in this dissertation explored the interaction between an adatom and a fcc(100) surface during the migration of the adatom via the bridge hopping and atomic exchange mechanisms. In order to effectively map out the migration of the adatom, it is necessary to have a realistic physical picture of the distortions induced in the lattice with a minimum of active atoms in the surface.

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