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Argon and neon trapping near copper surfaces

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Abstract. The binding energies of argon and neon impurities trapped below copper surfaces have been studied using a two-component effective-medium theory. The impurities are placed at various interstitial and substitutional sites and at divacancies within the first few surface layers, and the local energy minima as well as diffusion paths have been calculated taking into account full relaxation of the copper atoms. The results differ clearly from those obtained for bulk copper and are different for different surfaces. The results suggest that argon and neon are diffusing out from copper via a vacancy mechanism, with the help of a divacancy, or the impurity–vacancy pair dissociates clearly below the surface layer.

1. Introduction

Properties of rare gases in metals can be studied using desorption spectroscopy [1–3]. Various peaks in the desorption spectra represent different trapping sites of the impurity atom. Helium penetrates deep into the lattice and diffuses fast [2]. Consequently, the helium desorption spectrum is governed by trapping at defects in the bulk and the surface has a minor role. In contrast, the heavier rare gases, neon and argon, have a small penetration depth, and indeed several features of the spectrum have been interpreted as coming from trapping sites in the immediate vicinity of the surface [3, 4]. When using the desorption technique in studying neon and argon in metals, it is thus essential to study possible surface traps of these impurities.

In this paper we report on theoretical studies of the energetics of neon and argon within the first few atomic layers below a copper surface. We use the effective-medium theory (EMT) to describe the interatomic interaction [5–9], and calculate surface relaxations, activation energies for migration and desorption, activation energies for implantation and binding energies at vacancies. The results show that (i) the surface states can indeed be important in analysing the desorption spectra of neon and argon, (ii) the vacancy-assisted diffusion is important in the cases of neon and argon, and (iii) the activation energies are dependent on the surface geometry.

The paper is organized as follows. Section 2 specifies briefly the effective-medium theory that we use and describes the type of calculations done in this work. In section 3 results are given for impurity migration. Section 4 describes the results for the dissociation of a vacancy–impurity pair and section 5 gives the results for the dissociation of divacancy–impurity pairs. Vacancy migration is discussed in section 6 and conclusions are given in section 7.

2. Theoretical methods

The systems under study are so large—about one thousand movable copper atoms—that commonly used *ab initio* molecular dynamics methods [10, 11] are still too demanding and we have to use model potentials. In studying metal surfaces, however, it is essential to go beyond a pairwise interatomic interaction to account for the correct relaxation of metal atoms at the surface [12, 13]. Several reliable many-atom potentials have been developed during the last decade [14]. In the present work we use the effective-medium theory, where all but one of the parameters needed are computed from the embedding energies of atoms in a homogeneous electron gas (one parameter cannot be computed accurately from first principles but is used to fit the experimental elastic constant C_{44} [7]). It is important that we do not have to rely more on adjustable parameters, since in the present case we apply the model for impurities near a metal surface, i.e. to a system for which there are no direct experimental results. Moreover, for helium in bulk copper the method gives results in good agreement with the experimental ones [9].

The two-component extension of the EMT and the computational method is described in detail in references [6, 7] and [9]. In short, we calculate the energetics of an impurity atom by letting the surrounding metal lattice relax from the lattice sites. The two-component EMT is essentially a nearest-neighbour formalism, the cut-off radius of the interaction being about 3.1 Å. The total number of dynamical atoms in each simulation was about 700, with the consequence that all host atoms were allowed to move within a distance of at least three lattice constants from the impurity atom (to any direction). In calculating a diffusion path, the position of the impurity atom was also fixed. The migration energies were determined by calculating the total energy at several fixed impurity atom positions along the most likely diffusion paths.

In this work we studied neon and argon impurities close to the following surfaces of fcc copper: [100], [110], [111] and [340]. The first three are common low-index surfaces whereas the last one represents a stepped high-index surface. It was selected since there exist recent thermal desorption measurements for that surface [3]. Some results are presented also for the [210] surface.

3. Interstitial migration near the surface

In bulk copper the energetically preferred interstitial site for helium, neon and argon impurities is the octahedral site [9]. Helium and neon atoms reside in the centre of the interstitial site whereas the optimum site for argon is about 0.5 Å away from the centre of the octahedral site. The migration energy of the interstitial helium atom is about the same whether the migration goes through a tetrahedral site or directly from an octahedral site to another site. Neon ‘prefers’ diffusion through a tetrahedral site whereas argon ‘prefers’ direct diffusion from an octahedral to another octahedral site [9].

The present calculations were started by placing an argon or a neon atom at an octahedral site about five atomic layers below the surface for the low-index surfaces and in the 19th one for the [340] surface. Then the atom was moved towards the surface through octahedral interstitial sites by small steps. Note that this diffusion path is not always perpendicular to the surface, but follows the lowest-energy path. At every step the total energy was minimized by relaxing the copper lattice around the impurity. The resulting energies along the diffusion paths are shown in figure 1 for [100], [110], [111] and [340] surfaces.

Like in the bulk [9], the minimum-energy site for argon is an off-centre octahedral site while the neon atom ‘prefers’ the centre of the octahedral site. However, the depth of

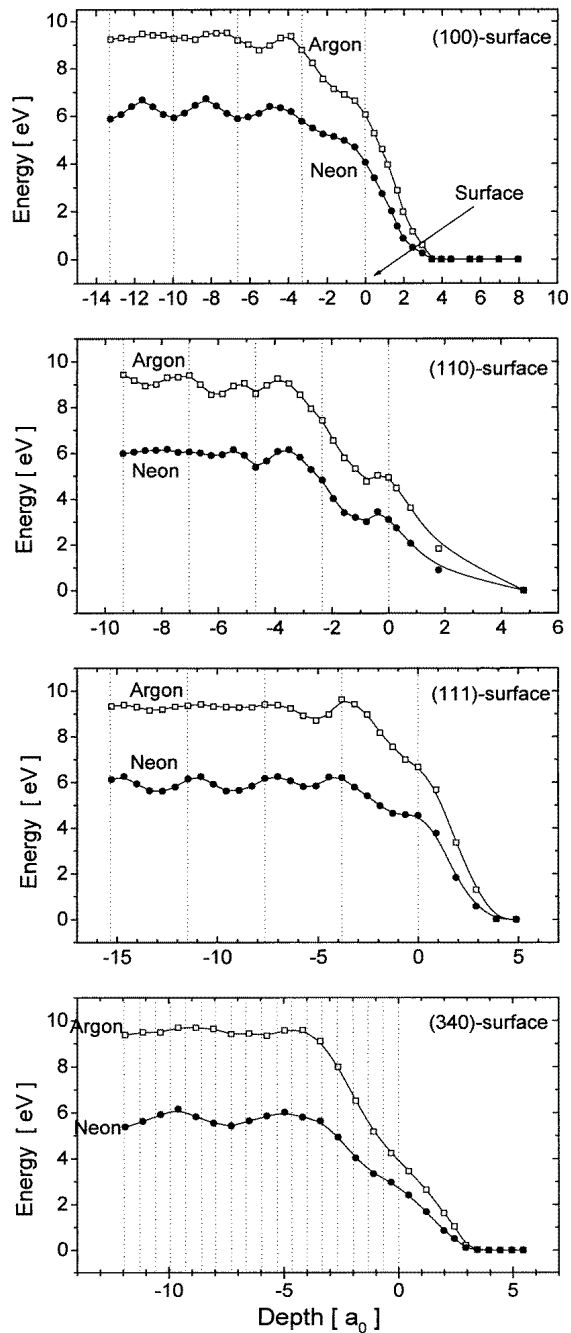


Figure 1. Potential energies when neon and argon atoms are moved from an interstitial site in the bulk to the surface through octahedral sites. The distance is given in units of the Bohr radius ($a_0 = 0.529 \text{ \AA}$). The lattice planes are shown as vertical lines. The top figure shows the result for the [100] surface, the second that for the [110] surface, the third that for the [111] surface and the fourth that for the [340] surface. The activation energy for implantation is the energy difference between the vacuum and the first maximum.

the energy minimum and the height of the energy barrier between adjacent minima depend drastically on the depth at which the impurity is below the surface and on the surface in question. Even four atomic layers under the surface, the results can differ from those of the bulk. This is due to the long-range relaxation made possible by the surface: the host atoms can be pushed more easily toward the surface than in other directions.

In the case of the [100] surface an argon atom has the deepest minimum between the second and third layers, whereas neon shows a bulk-like behaviour, starting from the second layer. The impurities cannot be trapped between the first and second atomic layers at the [100] surface.

Table 1. Activation energies for ion implantation into the first trapping site under the surface for argon and neon at different surfaces. In the case of the [110] surface the energies are given for the first two trapping sites. The last column gives the first-atomic-layer (inward) relaxation relative to the ideal site.

Surface	ΔE_{neon} (eV/atom)	ΔE_{argon} (eV/atom)	Surface relaxation (%)
[100]	6.40	9.37	-3.59
[110]	3.44	5.04	-2.63
[110]	6.14	9.25	
[111]	6.23	9.64	-3.07
[120]	6.08	9.56	-2.63
[340]	6.03	9.60	-3.60

Table 2. The maximum energy barrier (eV) of the dissociation of a gas atom from a vacancy in different atomic layers close to the surface. A vacancy in the first atomic layer does not bind the gas atom. The dissociation energies for the impurity–vacancy complex in the bulk are 3.8 eV and 2.9 eV for neon and argon, respectively.

Atomic layer	[100] neon	[100] argon	[110] neon	[110] argon	[111] neon	[111] argon
2	1.3	0.9	0.6	0.0	3.0	2.9
3	3.6	4.3	2.9	3.3	4.7	6.0
4	4.9	6.5	4.7	5.4	5.3	6.8

In the case of the [110] surface both impurities have a weak trapping site between the first and second atomic layers. The activation energy from the vacuum to this trap is several eV smaller than for the deeper traps. It could then be possible to implant low-energy impurities in these traps. However, impurities diffusing from the bulk to the surface are likely to get enough kinetic energy to pass this site without getting trapped. In the [110] surface, the diffusion path from an octahedral to another octahedral site is perpendicular to the surface. This straight channel enhances the migration of neon when it is deeper than in the third layer. The effect is smaller in the case of argon.

In the case of the [111] surface the first trapping site is between the second and third atomic layers. Neon is more strongly trapped below the third layer whereas argon is most strongly trapped below the second layer. Note that in the case of argon the bulk behaviour is not reached at the site of the fifth atomic layer, but that the diffusion path is nearly barrierless between the fifth and third layers. This is due to the strong relaxations caused by the argon atoms in the vicinity of the surface.

It is interesting to note that the behaviour for neon and that for argon near the low-index

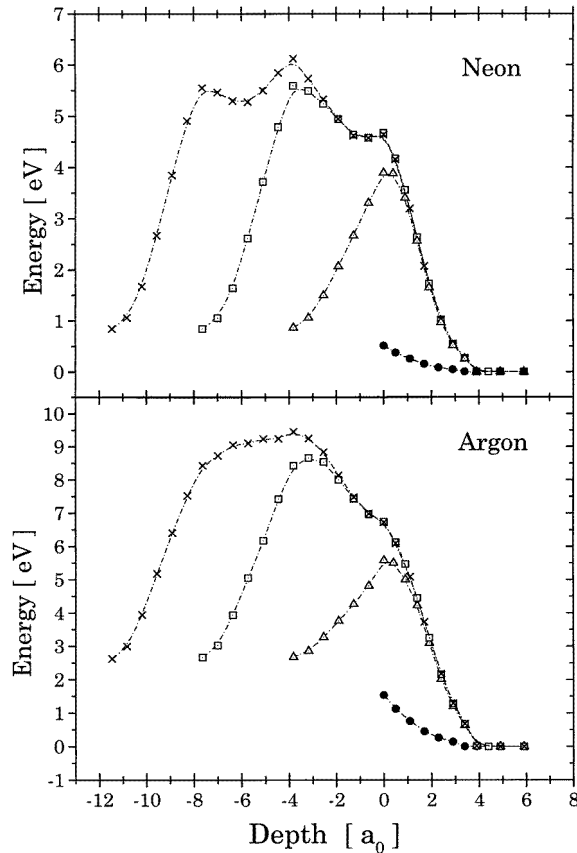


Figure 2. Minimum-energy curves for the dissociation of argon and neon trapped in first-layer (black dots), second-layer (triangles), third-layer (squares) and fourth-layer (crosses) vacancies at the [111] surface. The depth is given in units of the Bohr radius ($a_0 = 0.529 \text{ \AA}$). The starting point of each curve is at the centre of the vacancy.

surfaces are nearly opposite. In the cases of [100] and [111] surfaces, neon recovers the bulk behaviour soon whereas argon has a nearly barrierless path between the fourth and second layers. In the case of the [110] surface the result is the opposite. There is no simple explanation for this behaviour since it results from relaxations of the host atoms along the different diffusion paths on different surfaces. Note that the diffusion paths shown in figure 1 are not the shortest paths perpendicular to the surface, and that the argon atom 'prefers' an off-centre position in the octahedral site.

The last surface studied is a high-index surface, [340]. This is a stepped surface consisting of the [110] terraces and steps parallel to the [001] direction. The packing density of the atomic layers (defined as layers parallel to the surface) is significantly lower than in other surfaces studied and consequently the distance between the atomic layers is small. In figure 1 (lowest panel) the impurity atom is initially in an interstitial site at the 19th atomic layer. The impurity atoms are only slightly trapped at the interstitial sites near the surface. In the case of the stepped surface there are several possible routes to the surface. All of these were studied, and figure 1 shows those corresponding to the lowest energies.

The minimum energy that an ion should have in order to get implanted is the barrier

height from the vacuum to the first maximum below the surface. This activation energy for different surfaces is given in table 1. In the case of the [110] surface the results are given for the first two binding sites. The table also includes results for the [210] surface. In all cases the relaxation of the outermost surface layer of the undisturbed surface is inwards, as shown in table 1.

4. Escape from vacancies near the surface

Vacancies are effective traps for all rare gases. When impurity atoms are trapped at vacancies near the surface, the situation is more complicated than that in the bulk, since the relaxation around the vacancy–impurity complex is larger. The relaxation depends on the packing density of the surface in question. Consequently the binding energies depend on the depth where the vacancy is located, and differ from surface to surface.

Figure 2 shows potential barriers for the dissociation when argon or neon atoms are trapped at first-, second-, third- and fourth-layer vacancies under a [111] surface. The escape barrier for the second-layer vacancy is higher for neon than for argon. This is expected in view of the bulk results for the migration and dissociation energies [9]. However, the results for the escape barriers for escape from third- and fourth-layer vacancies are higher for argon. The reason for this surprising result is the large inward relaxation of the surface. It increases the electron densities at the first surface layers and, due to the repulsive interaction between the metal atom and the gas atom, the surface layers form a potential barrier to migration and desorption. The outward relaxations of the atoms surrounding the vacancy even increase this effect and consequently the impurity–vacancy binding energies can be larger near the surface than in the bulk. The diffusion barrier heights between the vacancy and the surface are collected in table 2. The energies given are the differences of the energies at the vacancy and at the maximum point of the path. Note that the maximum is not necessarily between the vacancy and the nearest interstitial site, but can also be closer to the surface.

In general, the energies are much larger than the dissociation energies of vacancy–impurity pairs in bulk, which are 3.8 eV for neon and 2.9 eV for argon [9]. This suggests that neon and argon atoms trapped at vacancies near the surface dissociate more easily towards the bulk than towards the surface, and eventually diffuse to the surface as interstitials or together with the vacancy.

A vacancy at the surface layer of the [111] surface is not a trapping site for neon or argon impurities. [110] and [100] surfaces are so open that the second-layer vacancy cannot yet trap an argon atom. Neon is trapped weakly at the second-layer vacancy in the [110] surface but not in the [100] surface. Deeper in, the trapping is strong like in the [111] surface.

Figure 3 shows characteristic results for diffusion paths from vacancies to the surface in the case of gas atoms trapped in eighth- and ninth-layer vacancies of the [340] surface. The path is generally not perpendicular to the surface but follows the minimum-energy curve. Note that the distance of the eighth-layer vacancy from the [340] surface is about the same as the distance of the second-layer vacancy from the [111] surface. For the [340] surface, the impurities at the vacancies in the first seven atomic layers are essentially free, except if the vacancy is situated just under a step of the surface. In that case the escape energies for vacancies in the fifth to seventh layers are 0.6–0.7 eV for argon and 0.7–0.9 eV for neon. The escape energies from the ninth- and eighth-layer vacancies are 3.00 eV and 2.90 eV for neon, and 3.40 eV and 3.14 eV for argon, respectively.

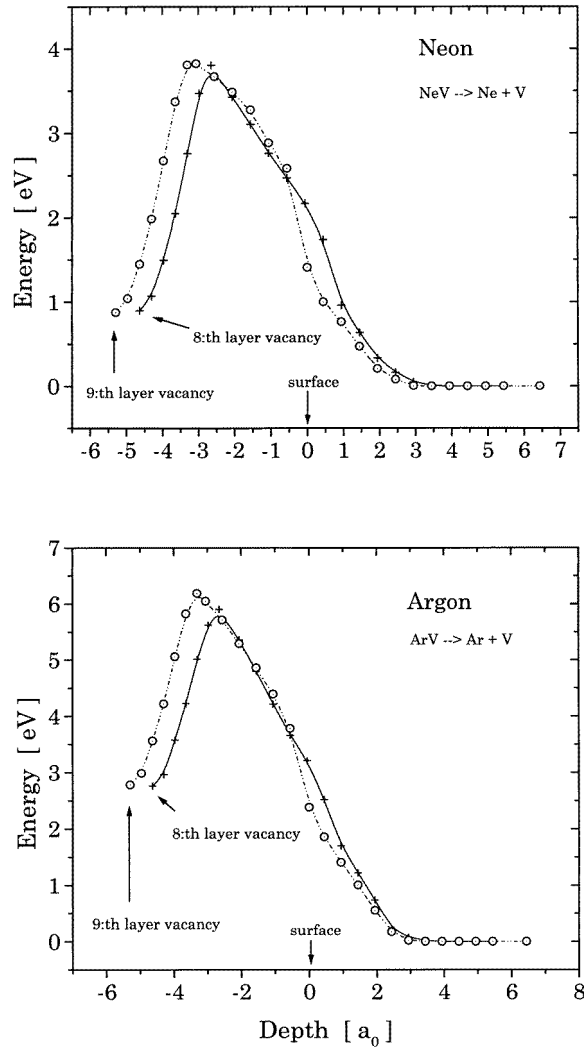


Figure 3. Minimum-energy curves for the dissociation of neon and argon trapped in eighth- and ninth-layer vacancies in the case of the [340] surface. The starting point of each curve is at the centre of the vacancy.

5. Trapping at divacancies near the surface

Large implantation energies or doses can create vacancy clusters filled with one or more gas atoms. In the case of bulk copper it was observed that a monovacancy can bind only one argon atom, but two neon atoms and up to three helium atoms [9]. Vacancy clusters are more effective trapping sites for neon and argon. In the present work we study only divacancies and restrict our calculations to divacancies below the copper [340] surface. The two vacancies are nearest neighbours in the [110] direction, nearly perpendicular to the surface.

First we studied a divacancy filled with one impurity atom. Figure 4 shows the energies of neon and argon atoms when they are moved through the divacancy and out from it to the

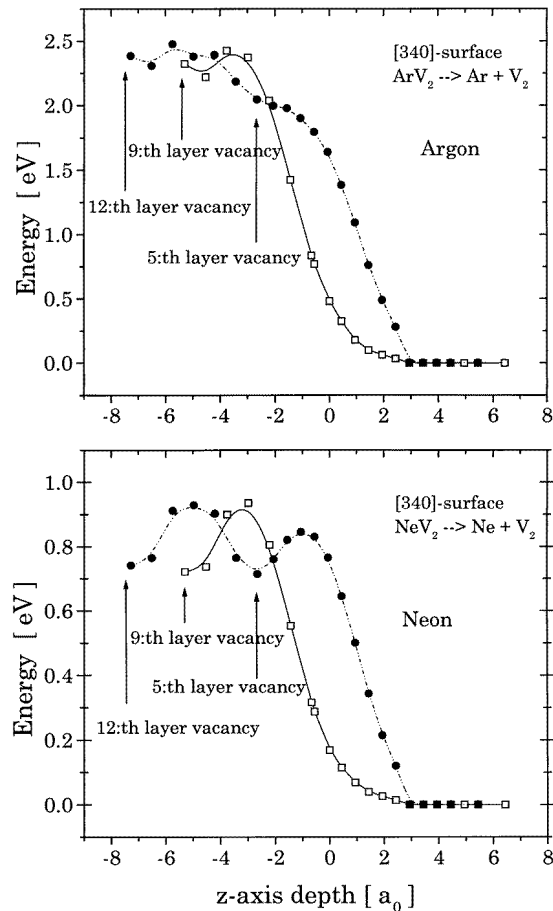


Figure 4. Minimum-energy curves for dissociation of the noble-gas impurity trapped in divacancies below the [340] surface. The vacancies of the divacancy are nearest neighbours located at the [110] direction (nearly perpendicular to the surface) in the second and ninth layers (curves marked with squares) or the fifth and twelfth layers (curves marked with black dots). The centres of the vacancies are shown.

surface along the lowest-energy path. In one case the vacancies of the divacancy are situated in the second and ninth layers just below the step at the surface (note that the second- and ninth-layer atoms are nearest neighbours at this surface and that the second-layer vacancy is at the surface). In this case there is only a very weak trapping site in the divacancy, with an escape energy of 0.20 eV for argon and 0.21 eV for neon.

As a second example, the two vacancies are in the fifth and twelfth layers below the surface step. Also in this case the argon curve only shows one weak minimum with an escape energy of about 0.17 eV near the centre of the twelfth-layer vacancy. The neon atom, on the other hand, has two nearly equivalent minima at the centres of the two vacancies, with escape energies of 0.17 eV (for the twelfth layer) and 0.13 eV (for the fifth layer).

Finally we studied the case where the divacancy is filled with two gas atoms and the gas atom closer to the surface was moved out to the surface. The result, again for the [340] surface, is shown in figure 5. The vacancies correspond again to nearest-neighbour sites,

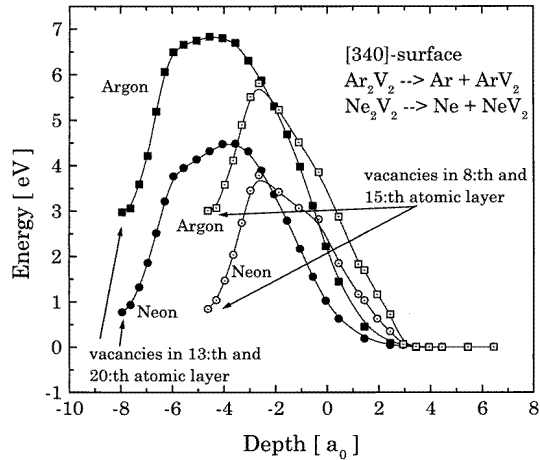


Figure 5. Dissociation energy curves for the escape of one gas atom in a doubly filled divacancy below a [340] surface. The vacancies of the divacancy are nearest neighbours located in the [110] direction (nearly perpendicular to the surface) at the eighth and fifteenth layers (curves marked with squares) or thirteenth and twentieth layers (curves marked with black dots). The curves start from the minimum-energy sites of the outermost impurity in the divacancy.

and the divacancy is oriented nearly perpendicular to the surface. The divacancy is able to bind two neon or argon impurities if the uppermost vacancy is at the eighth layer or deeper in the substrate. The escape energies of the first gas atom from the divacancy are 2.8 eV for argon and 2.9 eV for neon, if the divacancy is in the eighth and fifteenth layers. If the divacancy is deeper in the lattice, in the thirteenth and twentieth layers, the escape energies are larger, 3.8 eV for argon and 3.7 eV for neon. As in the case of a monovacancy, the maximum of the escape path is located near the surface and not in the immediate vicinity of the divacancy.

6. Vacancy migration

Pure vacancies in copper are already mobile below room temperature, and the experimental estimate for the migration energy is about 0.72 eV [15], based on the assumption that the stage III recovery is caused by vacancy migration. We calculated the vacancy migration energy in bulk by moving a nearest copper atom from a lattice site to a vacant site by small steps. At each step all other atoms were allowed to relax freely to their equilibrium sites. The resulting migration energy was about 1.3 eV, somewhat higher than the experimental estimate. This could be partly due to the static nature of the present calculations, since the top of the diffusion barrier is very narrow in our case. However, the estimates based on other interatomic interactions seem to indicate that the dynamical contribution is very small [17, 18].

The low activation energy of vacancy migration as compared to the energies needed to release neon and argon impurities from vacancies suggests that vacancy diffusion can be important in releasing these gases from the lattice. In particular, it is expected that a divacancy filled with only one neon or argon atom is mobile already at low temperatures.

7. Conclusions

The activation energies for implantation, shown in table 1, are high, as expected for rare gases, but rather insensitive to the surface in question. However, the interstitial diffusion of impurities is affected strongly by the surface at least down to the fourth layer of the low-index surfaces [111], [100] and [110], and even further in the high-index surface [340]. The activation energies of interstitial diffusion are of the same magnitude as in the bulk but are sensitive to the surface orientation, as seen in figure 1.

The escape energies for the impurities trapped by vacancies are large when the vacancy is not in the immediate vicinity of the surface, the maximum height of the escape path being located close to the surface. When the vacancy is near the surface, the activation energy is much lower. The results are again sensitive to the surface orientation and there are a wide range of activation energies depending on the depth of the defect and, in the case of a stepped surface, also on the position with respect to the step.

The high escape energies for argon and neon suggest that the escape from the lattice could be vacancy assisted. In particular, this is expected if the impurity is trapped in a divacancy. The impurity then jumps back and forth between two vacancies which are simultaneously migrating through the surface layers. The calculated vacancy migration energy, even though too large, is much smaller than the impurity–vacancy dissociation energy.

Finally, desorption experiments [3, 4, 16] have suggested that neon and argon have trapping sites near the surface. A persistent double peak in the measured spectra has been interpreted as trapping of argon atoms under the first few atomic layers of the surface. The present calculations indeed suggest that there are several trapping sites under the surface. However, they are very surface sensitive and cannot be the sole explanation of the persistent double peak seen in the desorption spectra.

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