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Vacancies below the (111) surface of Pd

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Density functional theory is used to investigate vacancies at or below the (111) surface of palladium and in the bulk. An accurate nonlocal pseudopotential for Pd based on relativistic all-electron calculations is employed. The interaction of the vacancy, a point defect, with a surface, a planar defect, is investigated. Also studied is the interaction between electronic structure and lattice structure around the vacancy. The vacancy-formation energy increases with the depth of the vacancy and with decreasing vacancy concentration. The ions surrounding a vacancy relax slightly into it, and the amount of relaxation decreases as vacancy depth is increased or as vacancy concentration is decreased. The primary electronic effects of the vacancy are a spillout of electrons into it and a strengthening of the bonds between the neighboring atoms that accompanies the inward relaxation.

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I. INTRODUCTION

The vacancy is one of the simplest defects in crystal structure and so represents a benchmark for experimental and theoretical understanding. The properties of vacancies are important for the kinetic behavior of metals; self-diffusion in monatomic metals is usually due to the propagation of lattice vacancies.[1] Vacancies are linked to the thermodynamic properties of metals as well; creating a vacancy increases the entropy of a lattice, for example. Unlike impurities, vacancies can be spontaneously created and, like impurities, become dynamic at sufficiently high temperature.

In addition to their role in diffusion, surface vacancies can also affect the reactivity of a metal. The perturbed electron density around a surface vacancy can alter the patterns of adsorption, and an adsorbate can even fill the vacancy.[2–4] Subsurface vacancies can diffuse to the surface, and our work shows that this is energetically favored; once there, they can participate in surface processes. A vacancy in a subsurface layer can also alter the electronic and atomic structure of a surface and thereby influence its chemistry.

Vacancies produce strong spatial variations in electron density: in a vacancy in Pd, the density drops rapidly to almost zero, decreasing to less than 1% of the average valence density over the nearest-neighbor distance (2.7 Å). In a sense, the vacancy is like a sphere of exposed surface embedded in the material and so presents similar challenges for density functional theory (DFT).[5,6] These challenges are well documented in the literature.[7–9] Carling *et al.* have computed an empirical correction to the vacancy-formation energy in aluminum and copper by comparing the surface energy for jellium calculated using DFT with the exact result.[7] (Since we are not primarily interested in the absolute size of the vacancy-formation energy, but rather in its variation with depth and concentration, we have not implemented these corrections.) Note also that there is some disagreement in the literature, with some authors finding that using the generalized gradient approximation (GGA) brings vacancy energies for Al and Cu into good agreement with experiment.[10–12]

When a vacancy is formed, the surrounding material reacts both electronically and elastically. Our goals include an investigation of the interaction between electronic and elastic properties in the presence of a vacancy, as well as the length scale of the perturbation to the electronic and atomic structure caused by the vacancy. Both the electronic and elastic properties of a vacancy are affected by proximity to a surface, and we will address the question of how these two types of defects interact. It is also of interest to determine how far below the surface a vacancy can be and still have significant effects on the surface or, equivalently, to determine the depth at which a subsurface vacancy begins to behave like a bulk vacancy.

Bonding in palladium is interesting because of the mixing between d and s levels that occurs in the solid. The ground state of the atom is $d^{10}s^0$, and if the atoms in the solid were to retain this state, then there would be no net bonding. Therefore all the bonding in the solid is due to promotion of electrons from d to s. It is of interest to ask what the presence of a vacancy does to this crossover. Palladium is of practical interest for its catalytic properties, with uses in automobile catalytic converters and fuel cells, for example. These catalytic properties are sensitive to small surface perturbations, e.g., alloying, particle-substrate interactions, or defects in metal structure.[13,14] We want to know how the presence of vacancies influences the catalytic behavior of Pd.

In this paper we study how the (111) surface of Pd is perturbed by vacancies. More specifically, we study vacancies at or below the Pd (111) surface, as well as in bulk Pd, and compute how their properties vary with depth and planar concentration. Additional motivation for this study comes from the recent scanning tunneling microscope (STM) studies that show anomalies beneath the (111) surface of Pd.[15] It is possible that the anomalies of Ref. 15 are caused by subsurface vacancies, so studying the signatures of subsurface vacancies is of value.

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Vacancies in bulk Pd have been the subject of considerable theoretical interest,[9,16] and recent studies have calculated the variation in vacancy-formation energy across the transition metal series.[8,17] These studies, all of which use unrelaxed ionic spacings, find reasonable agreement with experiment. To our knowledge, surface and subsurface vacancies in Pd have not yet been studied, although there has been theoretical work on surface vacancies in other metals.[18]

The plan of the remainder of the paper is as follows. In Sec. II we briefly summarize our methodology, and in Sec. III we present the results of testing it on bulk Pd and the (111) surface. Section IV contains our results for vacancy-formation energies. We discuss the effects of vacancies on bonding and charge density distributions in Sec. V and the ionic relaxation surrounding a vacancy in Sec. VI. We present our conclusions and outlook for future work in Sec. VII.

II. METHODOLOGY

All the calculations in this investigation were performed using density functional theory with a plane-wave basis.[5,6] The pseudopotential approximation was used to model the interaction of valence electrons with core electrons and nuclei.[19–21] The electron wave functions were relaxed with a blocked Davidson method,[22] accompanied by density mixing. The exchange-correlation functional was approximated by the form of Perdew *et al.* of the generalized-gradient approximation.[23]

A designed nonlocal pseudopotential[24,25] for palladium, based on relativistic all-electron calculations,[26] was constructed for this project. One might expect that relativistic effects would be negligible for a $4d$ metal like palladium. However, we find relativistic shifts of around 0.5 eV in atomic eigenvalues, and we judge these to be significant enough to require relativity to be incorporated. The ground state ($d^{10}s^0$) and first two excited states (d^9s^1 and d^8s^2) are excellently reproduced by the pseudopotential, with eigenvalues within 15 meV of the all-electron calculation and integrated tail norms within 1 millielectron. This agreement means that promotion of electrons from d states to s states will be given an accurate energy cost and that the atomic size will be well represented for all states.

III. PROPERTIES OF BULK Pd AND THE (111) SURFACE

We tested our pseudopotential by comparing our results to the known properties of bulk palladium and the (111) surface. Using 28 irreducible k points in the first Brillouin zone of the primitive fcc cell, we calculated a lattice constant of 3.86 Å and a bulk modulus of 0.178 GPa, both within about 1% of the experimental values of 3.89 Å and 0.181 GPa, respectively.[1] The cohesive energy was determined to be 4.05 eV, within 4% of the experimental value of 3.89 eV; this excellent agreement can be attributed to our use of the GGA. The surface energy was computed to be 0.68 eV/atom, in reasonable agreement with the reported values of 0.52 eV/atom from Pallassana *et al.* using DFT and the GGA (Ref. 27) and 0.77 eV/atom from Skriver and Rosengaard using the local-density-approximation (LDA) and linear-muffin-tin-orbital methods.[28] All of these theoretical results are low compared to the experimental value of 0.84 eV. A similar underestimate of the surface of energy in Al is what prompts Carling *et al.*[7] to compute corrections to vacancy-formation energies. We found that the top layer relaxation was negligible (less than 0.1% contraction) which is consistent with the experimental result of 0.9% ± 1.3% expansion[29] and with some other DFT calculations,[30,31] although other results differ.[27,32]

TABLE I. Vacancy-formation energies (in eV) as a function of layer and planar concentration (C).

C	1/4	1/6	1/8	1/9
Layer 1	0.92	0.97	0.95	1.03
Layer 2	1.18	1.19	1.18	1.22
Layer 3	1.25	1.25	1.26	1.29
Bulk	1.34	1.35	1.29	1.34

IV. VACANCY-FORMATION ENERGY

The energy cost to form a vacancy can be calculated as the energy of a slab with a vacancy plus the energy of a bulk atom minus the energy of a pure slab with no vacancy. To optimize error cancellation, the energies of the slabs with and without vacancies were computed using supercells with the same number of atoms per layer, the same fast Fourier transform (FFT) grid, and the same set of k points.

To study vacancies at or below the (111) surface, we use supercells with five layers of palladium and five layers of vacuum. For each, a vacancy was placed in one of the top three layers. For cells with vacancies in the first or second layer, the two bottom layers of the slab were held fixed with bulk spacings. For cells with vacancies in the third layer, the bottom layer of the slab was held fixed. The concentration of vacancies in the (111) plane was varied by changing the number of atoms in each layer of the supercell. The geometries used were $c(4\times2)$, $\sqrt{3}\times2\sqrt{3}R30°$, $p(2\times4)$, and $p(3\times3)$, producing planar concentrations of 1/4, 1/6, 1/8, and 1/9. To check convergence with respect to the number of layers, the vacancy-formation energy for the $c(4\times2)$ cell with seven layers and a vacancy in the second layer was computed and found to agree with the five-layer result of 1.18 eV. Convergence with respect to k points to the level of 1 meV per 20-atom cell was achieved for the $c(4\times2)$ cell with 64 reducible k points (16 irreducible k points) in the first surface Brillouin zone; computations on larger cells were performed with the same k-point density. For studying vacancies in bulk, we used cells with three (111) layers of Pd and the same planar geometries as in the slab calculations. To check convergence with respect to the number of bulk layers, a five-layer supercell with four sites per layer was studied; it gave a vacancy-formation energy of 1.30 eV, 0.04 eV lower than the three-layer result.

Table I presents our results for the vacancy-formation energy as it varies with depth and planar concentration. The relatively large difference between the formation energy of a surface vacancy and the formation energy of a vacancy in the second layer can be partially attributed to the smaller coordination number of surface atoms. The difference in vacancy-formation energy between bulk and surface vacancies is similar to those found in Ref. 18 for Al, Cu, Ag, and Rh. The vacancy-formation energy continues to increase with increasing depth below the surface. This trend can be linked to the elastic properties of successive layers of the material. For example, consider the case of a vacancy in the second layer. Atoms in the top layer are relatively free to move downward into the vacancy, lowering the energy. In the bulk, atoms bordering a vacancy are bound to atoms on the other side and would have to stretch those bonds to move into the vacancy. This relative lack of freedom leads to a higher vacancy-formation energy. For a quantitative example, the energy change due to ionic relaxation for the $p(3\times3)$ five-layer slab with a vacancy in the first subsurface layer is -0.14 eV compared to -0.08 eV for the three-layer bulk cell with a vacancy. We also notice that the vacancy-formation energy converges rapidly to the bulk value and that the convergence is quicker at the lower concentrations. In other words, it takes more layers for the perturbation due to a high concentration of vacancies to be smoothed out.

For subsurface vacancies, there is a trend of increasing vacancy-formation energy with decreasing concentration. We find that at high vacancy concentration, whole planes of atoms can relax together. At low concentration only the atoms surrounding the vacancy relax, leading to some curvature in the layers bordering the vacancy and higher vacancy energies. In the bulk calculations, performed at fixed volume, planar relaxation is not favored even at high density, since it would stretch interlayer bonds.

Our result for the vacancy-formation energy in bulk Pd, at the lowest concentration, is 0.4 eV lower than the experimental results,[33,34] which are in the range of 1.7–1.8 eV. Other DFT calculations[9,16,8,17] give values closer to the experimental result but still consistently low. Part of the difference between our results and previous results is attributable to the energy change accompanying ionic relaxation, which we include where previous authors have not. Note that the fractional deviations of our surface energy and our bulk vacancy-formation energy from their respective experimental values are approximately equal (-21% and -23%, respectively). This suggests that the errors have the same source and that a correction using the techniques of Carling *et al.*[7] might bring our results into agreement with experiment. On the other hand, the supercells that we have used are small and at least part of the deviation may be due to that.

V. BONDING

The *d* and *s* bands in Pd are very close in energy and therefore mix. The partially filled *d* band can then undergo covalent bonding. In this section, we address the question of how the presence of a subsurface vacancy affects the bonding between the surface atoms that border it.

We expect that a subsurface vacancy, either in the second or third layer, will affect the charge distribution in the surface layer. The valence charge density for a surface layer above a vacancy in a relaxed slab is shown in Fig. 1, with the corresponding plot for a defect-free surface shown in Fig. 2. Comparing the two figures, we see that after relaxation the surface charge density of the system with the vacancy is higher than that of the defect-free system. The electronic rearrangement that follows the inward relaxation of the atoms overcompensates for the loss of electrons brought about by the vacancy: after relaxation the valence electron density above the vacancy is 7% higher than at the corresponding hcp site in the defect-free slab. We also see that after relaxation the atoms rebond more tightly: the valence charge density at the bridge site, midway between two of the atoms above a vacancy is 3% higher than at the corresponding

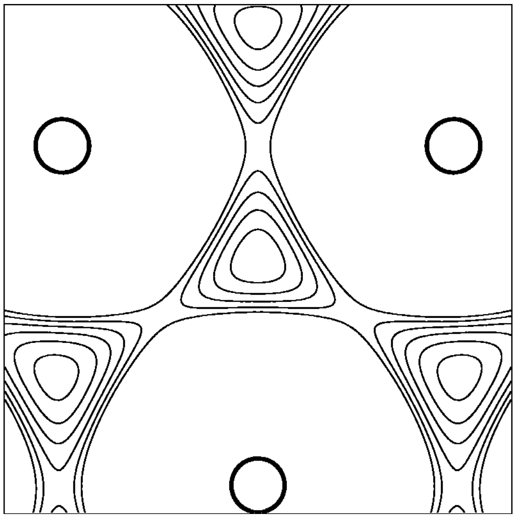

FIG. 1. Charge density contours for the (111) surface layer of a relaxed slab with second-layer vacancies at a concentration of 1/9 [the planar cell is $p(3\times3)$]. The plot is centered on the position of a vacancy. The contour spacing is 0.01 $e/\text{Å}^3$, the lowest contour at the center of the plot is at 0.13 $e/\text{Å}^3$, and the highest contour, closest to the nuclei, is at 0.17 $e/\text{Å}^3$.

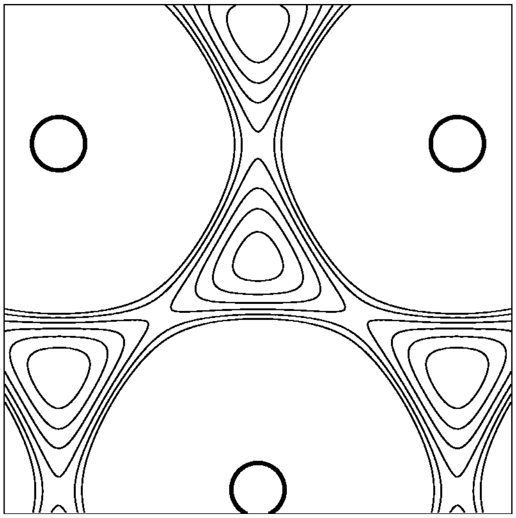

FIG. 2. Same as Fig. 1 for the case of a defect-free system, except that the lowest contour at the center of the plot is at 0.12 $e/\text{Å}^3$, one lower than in Fig. 1. The plot is centered on the hcp hollow site.

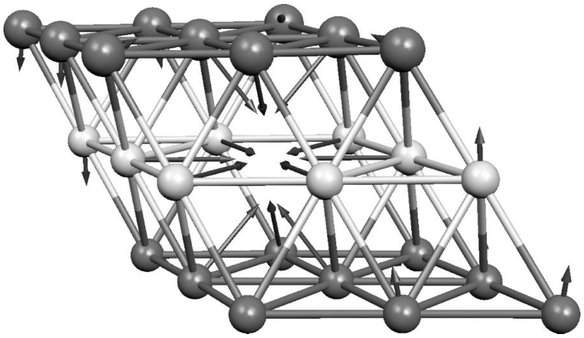

FIG. 3. Three (111) planes of atoms in bulk. The middle plane has vacancies at a concentration of 1/9. The arrows show the relative magnitude of the ionic relaxation, with the longest arrows corresponding to moves of 0.037 Å.

point in the defect-free slab. The density in the fcc hollow site is also affected, increasing by 3% over the defect-free slab. Note that this density increase is a result of the relaxation; our results for an unrelaxed slab show smaller densities at the hcp site and bridge site than in the defect-free case. The surface charge density above a vacancy in the third layer shows the same pattern to a lesser degree.

These pictures raise the interesting question of the difference in chemistry between a defect-free surface layer and a surface layer above a vacancy. We expect that the altered charge density will affect the bonding strength and/or structure of adsorbed molecules. In particular, we expect that the bridge and hollow sites will bind differently.

VI. IONIC RELAXATION

The changes in electronic structure caused by the creation of a vacancy affect the surrounding lattice structure in two principal ways: electron spillout and rebonding. By electron spillout we mean the process of electron density moving into the vacancy, thereby smoothing out the electron density and lowering the kinetic energy of the electrons. With respect to bonding, a simple *d*-band model would predict a strengthening of the bonds between the atoms surrounding the vacancy, the idea being that since the atoms have fewer neighbors to bond with, they will bond with their remaining neighbors more strongly. Bond strengthening and electron spillout both work to draw the surrounding atoms into the vacancy. The ionic movement influences the bonding in turn, with atoms that have moved closer to each other rebonding more strongly.

We consider first the case of vacancies in bulk, focusing on the case of the $p(3\times3)$ cell. In Fig. 3, we see that the nearest neighbors to the vacancy relax toward it. These relaxations are all approximately equal in magnitude, ranging from 0.032 Å to 0.037 Å. The ionic motions for the other bulk cells under consideration are similar. In the layer adjacent to the vacancy layer in Fig. 3, the ionic motion of the next-nearest neighbors to the vacancy is about 1/3 the size of that of the nearest neighbors. So the region of dislocation created by the vacancy extends to the next-nearest neighbors or to a distance of about one lattice constant.

We find that subsurface vacancies exhibit significantly different relaxations. The structural responses to vacancies in the first subsurface layer of the $c(4\times2)$cell and the $p(3\times3)$cell are shown in Figs. 4 and 5. The largest effect is that the three surface atoms that border the vacancy relax toward it, with the relaxation being bigger at the higher vacancy concentration. The dependence of the relaxation on concentration can be interpreted in terms of the curvature that it causes. At a vacancy concentration of 1/4, three-quarters of the atoms in the surface layer are nearest neighbors to a vacancy. For this case, the downward relaxation of the next-nearest neighbors to the vacancy is about 60% of that of the nearest neighbors. Evidently, at high subsurface vacancy concentration, it is energetically favorable for the whole surface layer to relax toward the vacancy layer nearly uniformly. Contrast that to the behavior of the $p(3\times3)$case, in which only 1/3 of the atoms in the surface layer border the vacancy. The downward relaxation of the next-nearest neighbors is less than 40% of that of the nearest neighbors; the other atoms in the layer relax even less. In short, in the $c(4\times2)$case the whole surface layer relaxes downward and in the $p(3\times3)$case the relaxation is smaller and creates curvature, a dimple, in the layer.

The atoms that border the vacancy in the same plane also have sizable motions, both in the plane and out of it. The

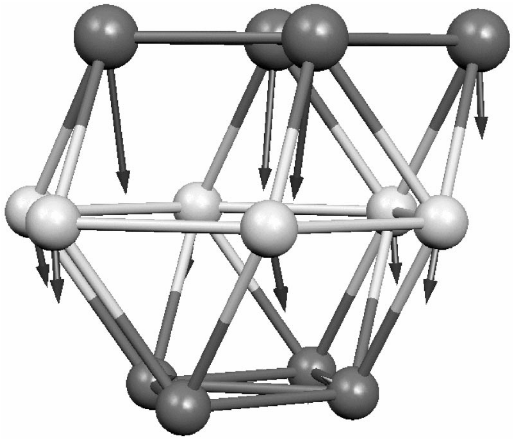

FIG. 4. The top three layers of a (111) slab. The second layer has vacancies at a concentration of 1/4. The arrows show the relative magnitude of the ionic relaxation, with the longest arrows corresponding to moves of 0.17 Å.

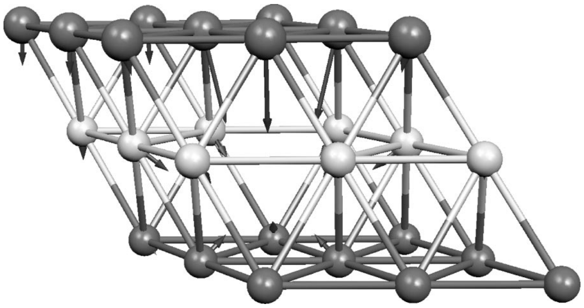

FIG. 5. Same as Fig. 4 for the case in which the second layer has vacancies at a concentration of 1/9; the longest arrows correspond to moves of 0.11 Å.

in-plane motions are comparable to those in bulk cells with the same planar geometry. The out-of-plane motion of these atoms is away from the surface, by about 0.07 Å for the $c(4\times2)$case and by about 0.02 Å for the $p(3\times3)$case. This downward motion reduces the spacing between the layers, thereby shortening and strengthening interlayer bonds. The ionic motions surrounding a vacancy in the second subsurface layer are similar to these, only somewhat smaller.

We can get more information about the region of dislocation induced by a vacancy by looking at the surface corrugation induced by vacancies in different layers. When there are vacancies at a concentration of 1/9 in the second layer, the induced corrugation of the surface ions is 0.080 Å. In the case of third-layer vacancies with the same concentration the surface corrugation is 0.018 Å. We conclude that for vacancies near a surface, the induced surface corrugation decreases quickly with vacancy depth, and the region of ionic dislocation extends to at least two adjacent layers.

VII. CONCLUSION AND FUTURE DIRECTIONS

In this paper we have examined vacancies in bulk Pd, at the surface, and in subsurface layers. We find that the vacancy-formation energy increases with depth of the vacancy, ranging from 1.03 eV at the surface to 1.34 eV for bulk (at a vacancy concentration of 1/9, the smallest studied). We find that some electron density moves into the vacancy and that the ionic response to the vacancy is an inward relaxation, accompanied by a strengthening of the bonds between atoms bordering the vacancy. Our findings are in accordance with the findings of Carling *et al.*,[7] suggesting that the GGA underestimates surface energies and vacancy-formation energies. We find that vacancies in the transition metal Pd share some of the characteristics of vacancies in the free-electron metal Al: inward relaxation of neighboring atoms[7,11,35] and the strengthening of bonds between them.[7,18] Interatomic bonds near vacancies in Pd are only strengthened as a result of nuclear relaxation; this is an interesting difference from vacancies in Al.

The effect of vacancies on neighboring layers is an important focus of this work. We predict that atoms in a surface layer above a vacancy relax into it and that the electron density in the hollow site above a vacancy is increased relative to a vacancy-free surface.

We also study the effect of varying the concentration of vacancies in a (111) layer. We find that for surface and subsurface vacancies, the vacancy energy increases slightly with decreasing concentration. At high concentrations, whole layers relax toward the vacancy and this behavior crosses over to local dimple relaxation at smaller concentrations.

This understanding of vacancies below the surface of Pd can lead to further experimental and theoretical studies of metal surface properties. Predicting the electronic and structural signatures of subsurface vacancies may enable the structural properties of metals to be probed in a nondestructive way. Finally, understanding the electronic and structural changes that a subsurface vacancy induces may help rationalize recent experiments that show a range of catalytic behaviors on a nominally clean surface.

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