

Ab initio vacancy formation energies and kinetics at metal surfaces under high electric fieldShyam Katnagallu ^{1,*}, Christoph Freysoldt ^{1,†}, Baptiste Gault ^{1,2} and Jörg Neugebauer ¹¹Max Planck Institut für Eisenforschung GmbH, Max-Planck- Str. 1, 40237, Düsseldorf, Germany²Royal School of Mines, Imperial College, Prince Consort Road, SW7 2BP, London, United Kingdom

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Recording field ion microscope images under field-evaporating conditions and subsequently reconstructing the underlying atomic configuration, called three-dimensional field ion microscopy (3D-FIM), is one of the few techniques capable of resolving crystalline defects at an atomic scale. However, the quantification of the observed vacancies and their origins are still a matter of debate. It was suggested that high electrostatic fields (1–5 V/Å) used in 3D-FIM could introduce artifact vacancies. To investigate such effects, we used density functional theory simulations. Stepped nickel and platinum surfaces with kinks were modeled in the repeated-slab approach with a (971) surface orientation. An electrostatic field of up to 4 V/Å was introduced on one side of the slab using the generalized dipole correction. Contrary to what was proposed, we show that the formation of vacancies on the electrified metal surface is more difficult compared to a field-free case. We also find that the electrostatic field can introduce kinetic barriers to a potential “vacancy annihilation” mechanism. We rationalize these findings by comparing to insights from field evaporation models.

DOI: [10.1103/PhysRevB.107.L041406](https://doi.org/10.1103/PhysRevB.107.L041406)**I. INTRODUCTION**

Crystal defects such as vacancies, impurities, dislocations, stacking faults, and grain boundaries significantly modify the mechanical, functional, or chemical properties of crystalline materials [1]. Mechanical or thermal processing steps create, alter, or annihilate such defects and hence allow for fine-tuning a material’s performance in principle. Yet, the precise relationships among processing-microstructure-properties remain unpredictable in most cases due to a lack of detailed understanding of the mutual interplay of different defects. Among such defects, the analysis of individual isolated vacancies remains broadly inaccessible despite their importance in material phenomena such as creep, dislocation motion and pinning, and diffusional transport. Populations of vacancies and their interactions with neighboring solutes can be indirectly characterized by, e.g., differential dilatometry and positron lifetime annihilation spectroscopy [2]. These techniques can measure a 10^{15} to 10^{19} cm^{−3} concentration of vacancies [3] in the material, which are usually encountered at high temperatures. The atomistic details of the structural and chemical interactions of the vacancies in materials can only be indirectly inferred. Many efforts have been pursued to achieve true atomic resolution—for instance, through field

ion microscopy (FIM) [4] and through advances in atomic electron tomography [5,6].

FIM was the first technique to image individual atoms on a metal surface [7] and it represents an alternative to electron-based techniques. FIM has helped in understanding the structure of crystalline defects such as grain boundaries, stacking faults, dislocations, and even vacancies [4,8–11]. FIM relies on ionization of an inert imaging gas near the surface of a specimen that is kept at electrostatic fields in the range of 1 to $5 \cdot 10^{10}$ V/m. Such intense electrostatic fields are achieved experimentally by shaping the specimen as a sharp needle with an end radius smaller than 100 nm. Needle specimens from crystalline materials often exhibit stepped terraces where major sets of crystallographic planes intersect the curved surface [12]. In FIM, the imaging of certain terraces is atomically resolved, due to the atomic scale corrugation of the electrostatic field [13–15], thus allowing one to image vacancies. Recent developments have led to three-dimensional (3D)-FIM, which involves recording the field ion images of a continuously field-evaporating specimen. Image processing algorithms deployed on a series of micrographs allow for a full 3D reconstruction [16], including the individual atomic positions [17–19], thereby enabling a quantification of the distribution and interaction of vacancies with solute elements [18,20]. Although 3D-FIM has the potential to estimate even small vacancy concentrations along with their spatial distribution, this capability has been questioned previously.

Early studies [4,21–23] showed that the vacancy concentration in some metals was much higher than the predicted equilibrium vacancy concentration. This led to the conclusion that most of the vacancies observed in FIM were artifacts that can originate from (i) field-induced etching in the presence of certain gases in the chamber, (ii) preferential field evaporation of solute atoms, (iii) reduction of vacancy

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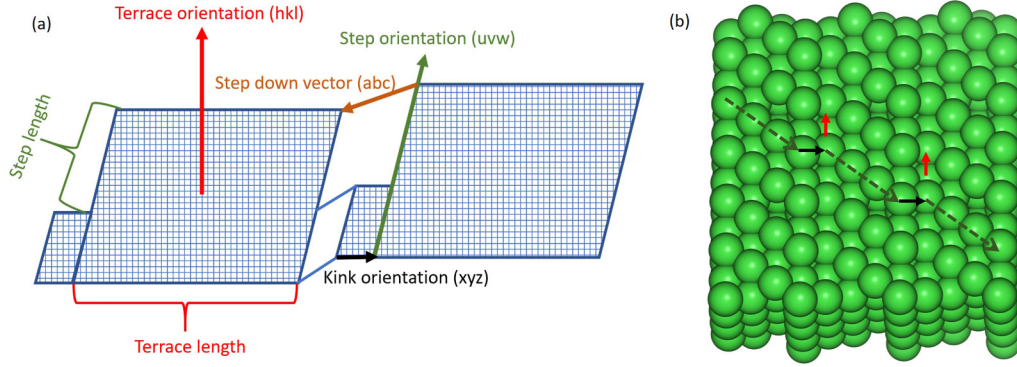


FIG. 1. (a) Schematic drawing of the high Miller index surface decomposed into relevant terrace, step, and kink orientations, and their lengths. (b) The nickel (971) surface composed of (100)-type terraces indicated by red arrows, with steps and kinks indicated with dashed-green arrows and black arrows, respectively. The atoms are colored according to the number of first nearest neighbors.

formation energy at the surface due to the high electrostatic field [24], and (iv) bombardment of the metal surface by polarized imaging atoms. Among these proposed mechanisms, the first two can be avoided by precisely controlling the experimental environment—i.e., by using high-purity imaging gas and ensuring the purity of the specimen. The fourth mechanism has only been suggested to occur in metals like gold [22], but not in refractory metals.

Here, in order to investigate the influence of the electrostatic field on the vacancy formation energy, we used density functional theory (DFT) calculations. Kohn Sham-DFT [25] forms the basis of modern *ab initio* electronic structure calculations and is widely applied in various fields of science [26]. To apply an electrostatic field efficiently in periodic boundary conditions, we use the generalized dipole correction method [27,28]. Stepped Ni and platinum surfaces with kinks were modeled with a (971) surface orientation. An electrostatic field of up to 4 V/Å was introduced on one side of the slab using the generalized dipole correction. We find that the vacancy formation energy *increases* with the application of an electrostatic field in both nickel and platinum. We also find the creation and suppression of energy barriers of atomic movements, under the application of a field. We show that such calculations can improve the confidence in extracting the vacancy concentrations and atomic environments from 3D-FIM.

II. METHODS

On the surface, steps and kinks are the relevant sites for field ion imaging and field evaporation due to their lower coordination. To represent such features using periodic slab models that are computable within DFT (100 to 1000 atoms), carefully chosen high-index surface orientations are employed. To set up the simulations, we designed a tool to generate metallic slabs of a high Miller index with selected terrace, length, and direction of steps and kinks, as shown in Fig. 1(a), based on the work by Van Hove and Somorjai [29]. This tool and all DFT calculations we discuss later are set up and analyzed in pyiron [30], which is an integrated development environment for atomistic simulations. We created an fcc nickel (971) surface (66 atoms), which has a (100)-type terrace with five-atoms-long steps and a one-atom-long kink

per surface unit cell. The slab is shown in Fig. 1(b). In order to apply an electrostatic field on one side of the slab, we use the generalized dipole correction implemented in the DFT library S/PHI/nX [27,31].

For the calculations, we use the projector augmented wave pseudopotentials taken from the VASP library and the Perdew–Burke–Ernzerhof (PBE) [32] exchange-correlation functional. We ensured a careful convergence with respect to the k points and the energy cutoff for plane waves to yield an accuracy of 10^{-3} eV in the relevant energies. A k -point sampling of $6 \times 6 \times 1$ and a plane-wave energy cutoff of 500 eV was used. Application of an electrostatic field usually induces a tensile Maxwell stress on the slab in the direction of the field. This then requires an additional convergence criterion—namely, the total thickness of the slab (9 Å) and the height of the fixed layers (4 Å) in the slab—to yield converged interlayer relaxations to within 0.1%. Similarly, for platinum (971), a slab containing 80 atoms with a height of 13 Å, an energy cutoff of 400 eV, and a k -point sampling of $6 \times 6 \times 1$ was used. Additional care must be taken for electronic occupancy smearing methods and widths used, as the charge distributions under these high electrostatic fields proved to be sensitive to them. We used Fermi-Dirac smearing with first-order entropy corrections with a width of 0.1 eV.

To evidence the influence of the electrostatic field, the vacancy formation energies (E_f) in nickel and platinum were calculated as a function of their lattice position within the slab. These values are obtained using the following equation:

$$E_f = E_{\text{vac}} - E_{\text{perf}} + E_{\text{bulk}}, \quad (1)$$

where E_{vac} is the total energy of the cell containing a vacancy, E_{perf} is the energy of the perfect slab without any defects under the same conditions, and E_{bulk} is the energy per atom in a bulk cell. The vacancy formation energies are also calculated for the same slabs without any electrostatic field.

III. RESULTS AND DISCUSSION

The vacancy formation energies are plotted as a function of the vacancy position within the slab with and without an applied electrostatic field of 4 V/Å for nickel and platinum [see Fig. 2(a) and 2(b), respectively]. The right end (10 Å and 14 Å) of each graph corresponds to the surface, and the left

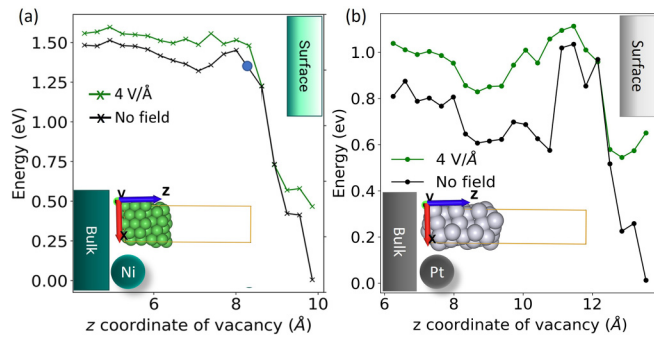


FIG. 2. Vacancy formation energy versus the position of the vacancy in the slabs with (green) and without (black) an electrostatic field in (a) nickel and (b) platinum. The insets show representative slab orientations for the plots, with the bulk region being inside the slab and the surface region toward the vacuum. The point of where vacancy spontaneously moves to the kink position is marked with a blue solid circle in (a).

one corresponds to bulklike positions inside the metal. For both metals, the vacancy formation energies are higher when the electrostatic field is applied—i.e., the electrostatic field does not facilitate the formation of vacancies. Right at the surface, the vacancy formation energy is raised by the field energy as the space previously filled by the atom becomes subject to the external field [33]. Deeper into the material, the field is increasingly screened, but a noticeable effect remains. This can likely be attributed to the induced Maxwell stress combined with the resulting material's mechanical response, which makes it difficult for vacancies to form compared to the field-free case. For platinum, the large site-to-site variations both with and without electrostatic field are related to the charge density redistributions occurring, even in absence of geometric relaxation, rather than due to unique structural relaxations for different vacancy positions (see Supplemental Material Figure S1 [34]).

The vacancy formation energy in the bulklike regions of the slab is compared with experimental and other DFT calculations in the literature. In this study, for nickel, the vacancy formation energy near the bulklike region of the slab without electrostatic field is 1.48 eV. Using a PBE functional, Nandi *et al.* [35] have reported 1.42 eV for nickel bulk and experimentally reported value through positron annihilation [36] is 1.73 ± 0.07 eV. For platinum, the vacancy formation energy in the bulklike region of our slab without an electrostatic field is 0.80 eV. Mattsson and Mattsson [37] reported a value of 0.68 eV as vacancy formation energy using PBE for platinum bulk. Whereas, the experimental reported values range from 1.24–1.45 eV [38] for platinum vacancy formation energy. The systematic discrepancy between the experimental and the *ab initio* calculated values could arise from the nonlinear temperature dependence of Gibbs formation energy of vacancies, which are not corrected in experimental data when extrapolating to 0 K [39], or from deficiencies in the functionals to reproduce accurate surface energies [35].

The nickel vacancy formation energy profiles in Fig. 2(a) exhibit a constant offset of ~ 0.085 eV ± 0.01 eV in the bulklike region of the slab. The higher vacancy formation energy under field can be attributed to the tensile strain from the

Maxwell stress ($\sigma_{zz} = \frac{1}{2}\epsilon_0 E_z^2 \approx 7$ GPa) induced by the electrostatic field E_z . To verify this hypothesis, we approximated the total strain in the slab as a uniaxial tensile strain extracted from the displacements of atoms in the slab along the z -axis (applied field direction). The average displacement along z -axis as a function of the z coordinate of atoms is shown in Supplemental Material Figure S2(a) [34]. This average strain (3.49%) is then applied to a 66-atom bulk nickel supercell oriented along the same high Miller index surface (971) direction used for creating the slabs. The difference in bulk vacancy formation energy under strain and strain-free cases is 0.11 eV, which is close to the 0.085-eV offset in our calculations. In contrast to the slab geometry in our simulations, the stress effect in experimental situations with curved surfaces will decay away from the surface, but only at a length scale comparable to the surface curvature. Hence, vacancy stability very close to the surface is more strongly affected than inside the tip. The volumetric effect of the vacancy is exemplified in Supplemental Material Fig. S2(b) [34]. It shows that vacancy formation energy increases as a function of uniaxial tensile strain applied to the bulk nickel. This indicates that the defect's excess volume tensor's interaction with the stress can in fact increase the vacancy formation energy. This effect would be similar for vacancies across all metals; thus, in general, application of an electrostatic field would make it difficult to form vacancies. Similar stress effects should be expected for other defects as well and should scale with the defect's excess volume (also called λ) tensor [40].

We then focus on a configuration for nickel in which a vacancy is positioned in a layer below the kink site, indicated by the blue circle in Fig. 2(a) and depicted in the inset in Fig. 3(a), with the considered nickel atom at the kink site in orange and the vacancy position as a white circle. The trajectory of the atom during its relaxation in the field-free case [Fig. 3(a)] has no discernible barrier. This vacancy-kink atom swap annihilates the vacancy, but retains the same high-index configuration as when the vacancy is on the surface when no electrostatic field is applied. However, upon application of a 4-V/Å electrostatic field, as shown in Fig. 3(b), an energy barrier of approx. 0.15 eV appears as the kink atom is moved toward the vacancy position following the same trajectory. We also plotted the mean displacements of the kink atom and the atom sitting next to the kink atom on the step [purple, in the inset of Fig. 3(b)]. This shows that only the kink atom is involved in the vacancy swapping. The energy barrier prevents the spontaneous vacancy annihilation from readily occurring. Additionally, the barrier for field evaporation would be very small and the kink atom is more likely to evaporate under such conditions, rather than participating in vacancy annihilation. It originates from the lower electron density of the kink atom, a consequence of its lower coordination, making it subject to a higher outward pulling force from the electrostatic field. The impact of the electrostatic field on the barrier height in the present case is analogous to the case of field evaporation [28], but with opposite sign. In field evaporation, a positively charged surface atom moves toward the negatively charged counter-electrode, and barriers generally *decrease* with increasing electrostatic field. In subsurface vacancy annihilation, the atomic movement is in the opposite direction, and hence barriers *increase*.

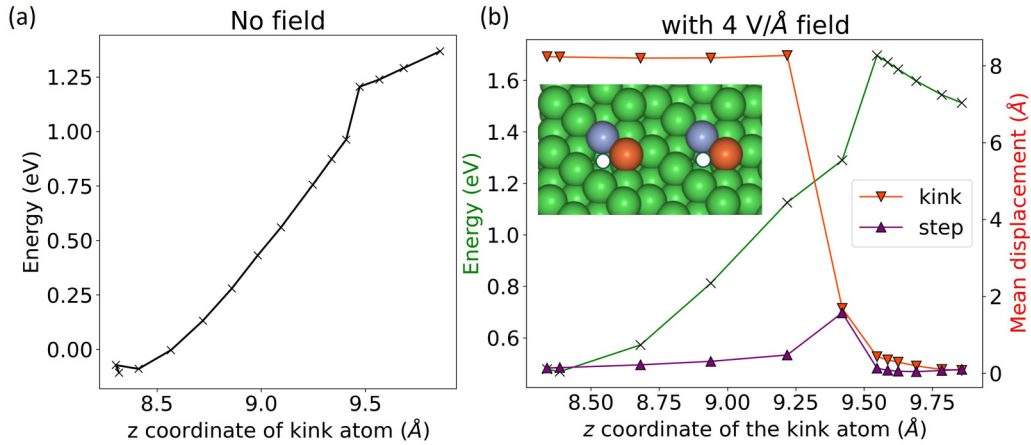


FIG. 3. (a) Potential energy landscape for a kink atom along the path to a vacancy position. Note that the kink atom can move into the subsurface vacancy without having to overcome a barrier. (b) Potential energy landscape for the same path in the presence of an electrostatic field. The inset shows the slab's atomic configuration repeated twice, with the kink atom in orange, the step atom in purple, and the vacancy position indicated by a white solid circle. The graph also shows the mean displacement of the kink atom and of the neighboring step atom.

Next, to investigate the effect of a solute atom on vacancy annihilation, we followed the same barrier calculations, now with a tantalum atom at the kink site of the nickel slab. We chose tantalum, as in our recent 3D-FIM study [18], tantalum was shown to be bound with a vacancy in a creep-deformed nickel-2 at% tantalum alloy. DFT calculations with this configuration showed that the tantalum atom also drops down to the vacancy position without the electrostatic field. Interestingly, when a 4-V/Å field is applied in the calculations, tantalum stays at the kink site, but the nickel step atom next to the tantalum drops down to the vacancy position, in contrast to our observation in pure nickel under field. This can be attributed to the presence of an energy barrier (0.3 eV) for the step nickel atom next to the tantalum atom, when no electrostatic field is applied. This barrier for the step atom is calculated by fixing the tantalum atom and is shown in Supplemental Figure S3 [34].

This contrasting behavior in the presence of tantalum can be explained by the electronic charge density difference for a nickel slab with and without field, and with the addition of a tantalum solute. Figure 4(a) and 4(b) shows, respectively, for the nickel and Ni-Ta slabs, the isosurfaces corresponding

to a $-2.0 \times 10^{-6} \text{ Å}^{-3}$ electron density difference, which corresponds to a net-positive charge. It can be seen that the step atom, indicated by the yellow arrow, develops a higher and wider net-positive charge in the pure nickel compared to when it is neighboring the tantalum atom. This is further illustrated through the sections in electron density difference taken along planes containing the position of step and kink atoms, shown in Fig. 4(a) and 4(b) for the nickel and Ni-Ta slabs, respectively. Only negative electron density differences (i.e., positive charges) are plotted for simplicity. The difference in the net-positive charge gained by the step atom, based on its chemical environment, can be attributed to the atom's electronegativities. Nickel has an electronegativity of 1.9—i.e., higher than 1.5 for tantalum [41]. Thus, when tantalum is present, nickel tends to have a higher electron density (Supplemental Material Figure S4 [34]) and can only gain a smaller net-positive charge when the electrostatic field is applied. This in turn leads to a smaller force (prior to relaxation) acting on the atom, and so it can swap its position with the vacancy, unlike when a nickel atom is present at the kink site. The field evaporation process itself is determined by the potential energy surface seen by the atom. However, the electrostatic

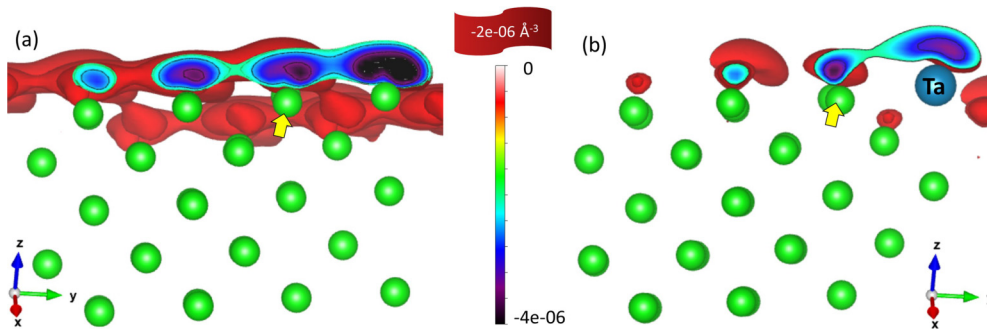


FIG. 4. Isosurfaces of $-2e-06 \text{ Å}^{-3}$ corresponding to an electron density difference due to the application of a field in a tilted (a) nickel (971) slab and (b) Ni-Ta (971) slab. Cross sections through the plane containing the step and kink atom in the nickel (971) and Ni-Ta (971) slabs are also shown in the isosurfaces. The position of the step atom is indicated by a yellow arrow, which shows that the step atom gains a smaller net-positive charge when tantalum is present next to it.

forces acting on atoms are relevant in the context of accessible surface geometries.

In summary, applying an intense electrostatic field generally increases the energy of vacancy formation in nickel and platinum, making the creation of artifact vacancies in FIM unlikely. The Maxwell stress generated by the electrostatic field slightly increases the vacancy formation energies also in the bulk. In configurations where a vacancy can spontaneously move to the surface, the application of the electrostatic field generates an energy barrier that can inhibit the exchange of the position with a surface atom. This mechanism for vacancy annihilation on the surface remains possible when a solute—here, the more electropositive tantalum—is in a kink site because of the decrease in charge density on the nickel atom. However, provided these extracted vacancy concentrations from FIM are statistically significant, as facil-

itated by developments of the FIM data extraction routines [19,42], these annihilations are unlikely to cause a substantial drop. This analysis can be extended further to other metal systems, based on the vacancy excess volume tensor and its interaction with the stress due to an electrostatic field. These simulations can improve the confidence of the extracted vacancy concentrations and structures through 3D-FIM.

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