

First-principles study of alloy stability and diffusion on aluminum alloy surfaces

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The stability of aluminum alloy surfaces has a critical influence on their ability to join to another material. This study employs first-principles density functional theory calculations to investigate the surface stability, configuration, and diffusion tendencies of alloying elements Mg, Si, Zr, and Sc on the crystal planes (001), (110), and (111) of an aluminum alloy. Utilizing asymmetric slab models, we introduce and apply an energy difference concept (ΔE^{2D}) to assess the stability of surface alloys relative to pure element covered surfaces. The findings reveal that surface stability is strongly dependent on both composition and atomic arrangement. Generally, mixed surface compositions, particularly a 50% coverage Al_2M_2 , exhibit enhanced stability. And the next nearest neighbor is favored over the nearest-neighbor position of alloying atoms which are precursors to nearest precipitates. An analysis of the diffusion paths indicates that Mg and Si preferentially segregate to the outermost surface layer with Mg more strongly, whereas Zr and Sc exhibit a lower driving force to diffuse towards the outermost aluminum surface.

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I. INTRODUCTION

Aluminum alloys are widely used structural materials with the performance directly influencing their durability in complex environments [1–3]. The surface of aluminum as the primary interface interacting with the external environment determines key properties such as the interfacial bonding with other materials [4–6]. The alloying elements can significantly alter the composition, structure, and properties of aluminum [7,8]. For instance, Al-Mg alloys are good for high strength and lightweight characteristics. Mg in aluminum shows multiple strengthening mechanisms, including solid solution strengthening, precipitation hardening, strain hardening, and dislocation substructure strengthening [9]. Similarly, Al-Si alloys exhibit a low coefficient of thermal expansion, excellent wear and corrosion resistance, and good mechanical properties across a wide temperature range. The formation of hard silicon phases in Al-Si alloys enhances their wear resistance [10]. In Al-Zr alloys, the formation of Al_3Zr phases increases the recrystallization temperature and thermal stability of the alloy, making it suitable for high-temperature environments. Trace amounts of Zr react with aluminum to form fine Al_3Zr particles, which act as heterogeneous nucleation sites during solidification, promoting grain refinement [11,12]. These particles, distributed at grain

boundaries, pin the boundaries and inhibit grain growth during high-temperature exposure or heat treatment [11,13]. Furthermore, in Al-Sc alloys, the addition of Sc exceeding 0.4 wt. % leads to the precipitation of Al_3Sc phases during solidification, significantly refining the grain structure and improving the alloy's strength and toughness [14].

Previous studies have shown the formation of Mg, Si, Zr, and Sc alloys. According to a systematic first-principles diffusion study [15], the binding energy between magnesium atoms and vacancies in face-centered-cubic (fcc) aluminum is nearly zero: Gradient-corrected density functional calculations with the PBEsol functional resulted in very low binding energy values of -0.006 eV with the projector-augmented wave method (PAW) and of 0.008 eV employing norm-conserving pseudopotentials (NCPPs). Those small values suggest that Mg substitution in fcc-Al is energetically favorable, but with formation energies close to zero. First-principles calculations within the generalized gradient approximation (GGA) reveal that the dilute impurity energy for silicon in aluminum is $+0.49$ eV per solute atom [16], indicating limited solubility. At the eutectic temperature (577°C), the α -Al phase can dissolve up to 1.65 wt. % Si (approximately 1.5 at. %), beyond which a two-phase mixture of α -Al and Si forms upon solidification [17]. The enthalpy change (ΔH) for the transformation of Al_3Zr from the $\text{L}1_2$ to the more stable DO_{23} structure is -1.72 mRy/at (i.e., -0.0234 eV/at). The formation energies of these ordered compounds are negative, indicating that compound formation is energetically favorable. Unlike silicon, zirconium is less likely to dissolve in aluminum and instead prefers to form distinct compound phases [18]. The formation enthalpy of the compound Al_3Sc at 0 K is -0.463 eV, suggesting that Al_3Sc is energetically more favorable and stable compared to the equilibrium crystal structures of pure Al and Sc [19].

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However, the vicinity of a surface introduces differences in properties compared to the bulk metal due to several factors. These include the reduction in atomic coordination numbers [20], changes in surface electronic structure [21,22], as well as surface atom relaxation [23] and reconstruction [24]. These phenomena lead to distinct surface characteristics that deviate from those of the bulk material. Despite the critical role of surfaces in determining material performance, traditional experimental techniques face limitations in revealing atomic-scale transformation mechanisms, particularly for surfaces that are only a few atomic layers thick [25,26]. This makes it challenging to gain a deep understanding of the stability and behavior of such surfaces.

To address these challenges, first-principles calculations based on density functional theory are used here as a theoretical tool, and the surface properties of aluminum and its alloys have been extensively studied using supercell models, with a focus on both pure aluminum and multielement systems. For pure aluminum, the studies have employed symmetric and asymmetric slab models to investigate surface relaxation and surface energy. For symmetric aluminum slab structures with equivalent top and bottom surfaces, the surface energy can be calculated using Eq. (1) [27],

$$E_{\text{surf}} = \frac{1}{2A}(E_{\text{slab}} - E_{\text{bulk}}) = \frac{1}{2A}\left(E_{\text{slab}} - \sum_i n_i E_i\right). \quad (1)$$

Here, E_{surf} denotes the surface energy per unit area, A represents the surface area of the slab model, E_{slab} is the total energy of the aluminum slab, and E_{bulk} corresponds to the total energy of the bulk. The terms n_i and E_i refer to the number of atoms and the average energy per atom in the reference aluminum. For simulating larger surface areas explicitly, thinner, asymmetric slab models were used where the bottom layers are fixed at the ideal inner-slab distances and only the top surface is optimized. Following Ref. [28], the surface energy is calculated according to Eq. (2),

$$E_{\text{surf}} = \frac{E_{\text{slab}}^{\text{unrelax}} - n_i E_i}{2A} + \frac{E_{\text{slab}}^{\text{relax}} - E_{\text{slab}}^{\text{unrelax}}}{A}. \quad (2)$$

This formulation decomposes the surface energy into two contributions, the energy associated with creating two unrelaxed surfaces and the energy change resulting from the relaxation of the top surface only.

Previous results [29] indicate that the relaxed geometries and surface energies of Al(111) and Al(001) surfaces reveal that the Al(001) surface exhibits more significant relaxation and higher surface energy. Surface relaxation primarily affects the electrostatic potential distribution in the surface layer, while the internal layers exhibit electrostatic potential distributions similar to the bulk. Mulliken population analysis further indicated that surface atoms possess slightly higher electron densities compared to bulk atoms, with increased bond populations at the surface. Band-structure analysis showed that the conduction-band widths of Al(111) and Al(001) surfaces align with those of bulk aluminum, although surface state energies were slightly underestimated, and core-level shifts were overestimated [29,30].

For multielement systems with stoichiometric compositions, surface energy calculations have been conducted by

considering the total energy of the compound rather than individual atomic energies using Eqs. (1) and (2). For example, the surface energies of low-index NiAl crystals were determined by computing the total energy of NiAl [31], avoiding the partitioning of energy contributions from individual atoms. However, studies on the behavior of alloying elements at surfaces remain limited, primarily because the surface stoichiometry of alloys may deviate from the bulk stoichiometry, making the partitioning of energy contributions from individual alloying elements complicated. Sakong *et al.* [27] addressed this complexity by studying bimetallic surfaces, specifically Ag/Pt(111) and Ag/Pd(111). They constructed symmetric slab models without vacuum layers, incorporating surface deposition layers, as well as asymmetric models with relaxed surface layers, to determine the surface energies of asymmetric surface regions. The approach distinguished between bulk and slab formation energies and included corrections for the strain energy of pseudomorphic thin films in symmetric models without vacuum layers [27].

The present study aims to establish a method for describing surface stability by constructing asymmetric metal crystal slab models incorporating vacuum layers. Surface relaxation was performed for the alloy atoms in the slab model used in this study. This relaxation eliminates the need to consider effects like alloy layer compression and pseudomorphic alloy phases described in Ref. [27]. And we systematically investigated the influence of various alloying elements on the surface stability and their diffusion in the vicinity of the surface. The three primary crystal planes of face-centered-cubic aluminum—(001), (110), and (111)—will be considered. Al alloys with Mg, Si, Zr, and Sc are the examples chosen for presenting our approach. Using density functional calculations, the aluminum atoms in the outermost surface layer will be substituted to systematically examine the impact of doping elements on the surface stability of aluminum alloys. Second, possible diffusion intermediates of the alloying elements in the vicinity of the surface layers are investigated. The primary objective of this research is to provide a theoretical way to understand the surface alloy stability.

II. COMPUTATIONAL DETAILS

Density functional theory calculations were conducted using the plane-wave based package ABINIT (version 9.10.3) [32–35] to determine the total energies of aluminum in both bulk and slab structures. The exchange-correlation interactions were described using the Perdew-Burke-Ernzerhof (PBE) [32] generalized gradient approximation (GGA) functional. Norm-conserving pseudopotentials were employed to represent the ionic cores. The Kohn-Sham electronic wave functions were expanded using a plane-wave basis set with a kinetic energy cutoff of 815 eV to represent also the polarizable semicore states of the alloying atoms Mg, Sc, and Zr appropriately. Asymmetric slab models were created, including a supercell containing 7 atomic layers with a total of 28 atoms. The bottom three layers were fixed to the bulk positions, while the uppermost four layers representing the surface are relaxed within the structures. A vacuum layer of 30 Å is incorporated along the z -direction. The slab models corresponding to the (001), (110), and (111) crystallographic

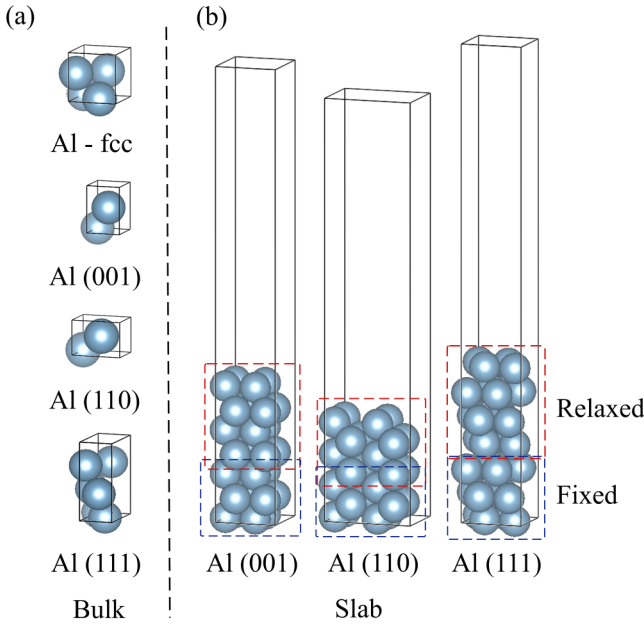


FIG. 1. (a) Aluminum bulk crystal structures applied specific transformation matrices from fcc aluminum. (b) Crystal structures of aluminum slabs with three different surface planes (001), (110), and (111). The atomic positions of the bottom three layers within the blue rectangles are fixed, and the four top layers of atoms indicated by the red rectangles are relaxed.

orientations of a face-centered-cubic (fcc) aluminum unit cell were generated by applying specific transformation matrices $\begin{pmatrix} -0.5 & 0.5 & 0 \\ -0.5 & -0.5 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, $\begin{pmatrix} 0.5 & 0 & -0.5 \\ 0.5 & 0 & -0.5 \\ 0 & 1 & 0 \end{pmatrix}$, and $\begin{pmatrix} -0.5 & -0.5 & -1 \\ -0.5 & 0.5 & -1 \\ 1 & 0 & -1 \end{pmatrix}$ on the fcc aluminum lattice, respectively. The resulting bulk structures are oriented along the respective surface normal in the z -direction, as shown in Fig. 1(a). Supercells of dimensions $(2 \times 2 \times 3)$ for the (001) and (110) orientations, and $(1 \times 2 \times 2)$ for the (111) orientation were created from these optimized bulk structures. The final slab models shown in

Fig. 1 were generated by introducing the vacuum layer. Structural relaxation was then performed on these slab models, optimizing the nuclear positions of the top four surface layers while keeping the cell shape fixed.

Surface alloy systems were investigated by substituting surface aluminum atoms in the relaxed slab models with Mg, Si, Zr, and Sc atoms (denoted as M) as shown in Fig. 2. Various surface coverages from zero to complete substitution were considered. As depicted in Fig. 2, different surface structures can be found at 50% surface coverage. Specifically, three different configurations were identified for the (110) surface, two for the (001) surface and one for the (111) surface. These configurations correspond to different M - M interatomic distances: 4.05 Å for structure 1, 2.86 Å for structure 2, and 4.96 Å for structure 3. For all Al and Al-alloy slab calculations, the first Brillouin zone was sampled using a $6 \times 6 \times 2$ Monkhorst-Pack k -point grid. The electronic self-consistent-field (SCF) iterations were converged until the difference in total energy between consecutive steps was less than 2.7×10^{-6} eV. The ionic relaxation convergence criterion was set such that the maximum energy difference between successive relaxation steps was below 1×10^{-4} eV/at. In addition, spin polarization was disabled. See the Supplemental Material [36] for a detailed analysis of alloy atom Sc (see also Refs. [37] therein).

III. RESULTS AND DISCUSSION

A. Surface alloy stability

To evaluate the stability of a bulk aluminum alloy relative to the pure phases, the formation energy of the alloy system is calculated here and denoted as $\Delta E^{3D}(M_m\text{Al}_{N-m})$. This quantity defines the energy difference between the bulk alloy and a weighted composition average of the pure bulk constituents as shown in Eq. (3),

$$\Delta E^{3D}(M_m\text{Al}_{N-m}) = E_{\text{bulk}}(M_m\text{Al}_{N-m}) - \frac{m}{N}E_{\text{bulk}}(M_N) - \frac{N-m}{N}E_{\text{bulk}}(\text{Al}_N). \quad (3)$$

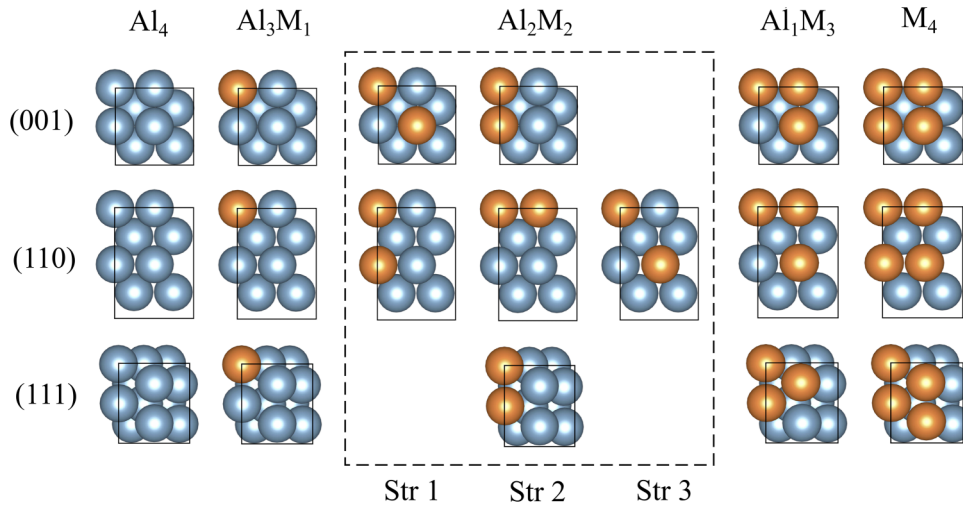


FIG. 2. The top views of the aluminum slab structures of the planes (001), (110), and (111) along the z -direction substituted by alloy atoms. When the aluminum surfaces are substituted by two alloy atoms (Al_2M_2), the (001), (110), and (111) slab models exhibit different surface structures (labeled as “Str1, Str2, and Str3”).

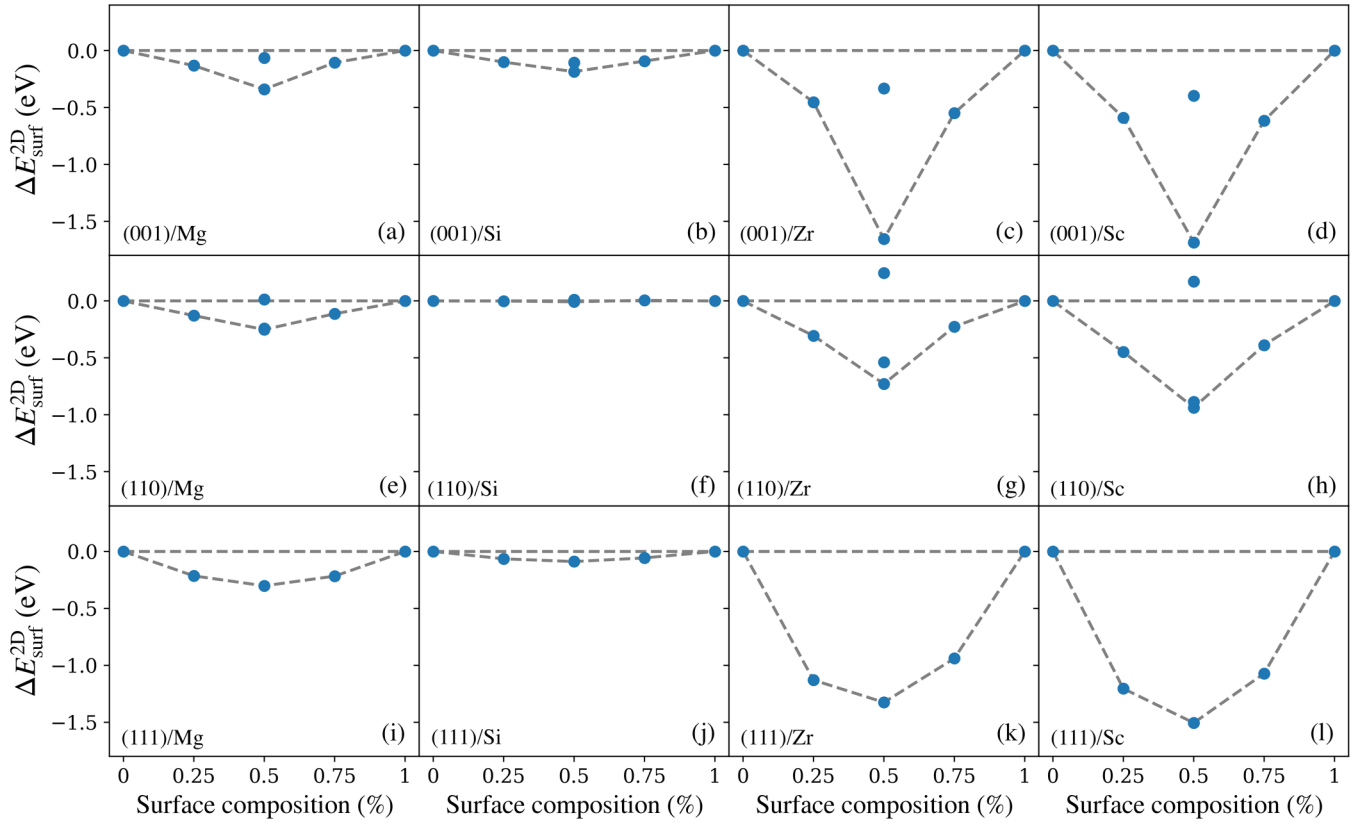


FIG. 3. The relations between the surface stability energy difference of alloying elements on the three aluminum planes with varying surface compositions of $\text{Al}_m\text{M}_{4-m}$ after structural relaxation. Specifically, the surface alloys (a) Mg, (b) Si, (c) Zr, and (d) Sc on the aluminum (001) crystal plane; (e) Mg, (f) Si, (g) Zr, and (h) Sc on the aluminum (110) crystal plane; and (i) Mg, (j) Si, (k) Zr, and (l) Sc on the aluminum (111) crystal plane.

Here, N represents the total number of atoms in the supercell, and m denotes the number of Al atoms substituted by M -type atoms. For the cases of the slab surface where surface aluminum alloys are substituted by the alloy atoms, which we define as two-dimensional (2D) surface alloys here, we analyze the stability relative to pure Al or M covered surfaces in the decomposed states. The energy difference of the surface alloy, $\Delta E^{2D}(M_{m'}\text{Al}_{n'})$, is calculated as in Eq. (4):

$$\Delta E^{2D}(M_{m'}\text{Al}_{n'}) = E_{\text{slab}}(M_{m'}\text{Al}_{N'-m'}) - \frac{m'}{N'}E_{\text{slab}}(M_{N'}) - \frac{N' - m'}{N'}E_{\text{slab}}(\text{Al}_{N'}), \quad (4)$$

where $N' = m' + n'$ is the total number of surface atoms, with m' and n' corresponding to the fractions of alloy M atoms and Al on the slab surface. Thus, the energy difference of the stability for a 2D surface is evaluated relative to a reference state which contains either a pure aluminum surface or a surface fully covered by alloying atoms in the first layer. A negative value indicates that the substituted surface structure is more stable than the reference state, with greater stability corresponding to more negative energy differences. The values of ΔE^{2D} obtained from the slab models are depicted in Fig. 3. The dashed line indicates the reference energy corresponding to a complete segregation of the surface alloy into areas of pure Al and fully M covered patches. All alloy

compositions with lower energy are thermodynamically stable. Connecting the lowest values of each composition indicates the phase stability of the surface alloy: if a convex hull is formed, all compositions are stable. Concave points indicate that the neighboring alloy compositions are stable. For example, if ΔE^{2D} , the energy difference of Al_3M_1 , lies below the line $\text{Al}_4\text{-Al}_2\text{M}_2$, the composition Al_3M_1 is more stable. Conversely, if the energy difference of Al_3M_1 lies above the line, the surface tends to decompose into phase-separated regions of pure Al and Al_2M_2 , indicating the instability of the surface composition Al_3M_1 .

In Fig. 3, the compositional ratios of different surface alloys Mg, Si, Zr, Sc, and the stability energy differences on various crystal planes are presented. Overall, all alloying elements exhibit the largest stability at 50% surface coverage with a minimum energy difference value at this concentration. Second, the largest values are obtained for Zr and Sc, whereas Mg and Si have more subtle influences, and the elemental trends are similar for all three surfaces. Yet, convex hulls are more strongly favored on the (111) surface, whereas (001) and (110) also exhibit concave parts of the hull. In detail, in the case of Zr on the (111) face, values of ΔE^{2D} for 25% and 75% surface Zr compositions lie below the line, indicating that these compositions are more stable relative to surfaces covered purely by the aluminum or by 50% Zr atoms. However, for Zr on the (001) face, the 25% and 75% surface Zr compositions are relatively less stable compared to the (111) face, with

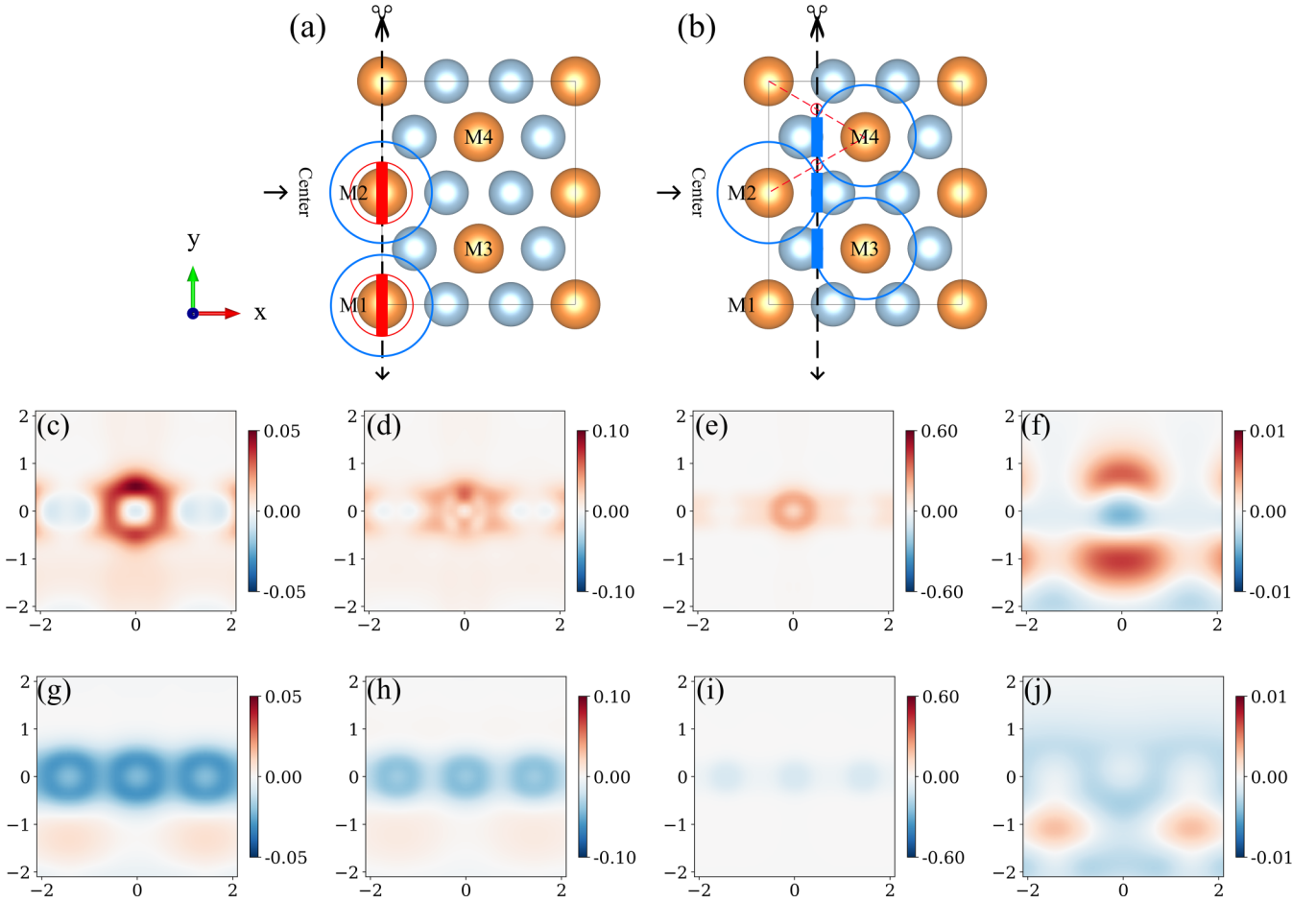


FIG. 4. The structure fully covered by alloy atoms with a cross-sectional cutting along the yz -plane: (a) the first cut passing through the centers of alloy atoms M located at $(0,0)/\text{\AA}^2$, and (b) the second cut passing through the midpoint (red dots) of the bonds between alloy atoms. Blue circle, valence sphere; red circle, sphere of semicore states. Red and blue bars indicate the regions on the differential density figures which are visibly modified by the alloying. The electron density difference maps of the yz -plane cross-sections for the first row cut through the centers of the alloy atoms: (c) Zr, (d) Sc, (e) Mg, and (f) Si, and for the second row they cut through the midpoints of the bonds between the alloy atoms: (g) Zr, (h) Sc, (i) Mg, and (j) Si. All density difference plots depict an area of 2.1 by 2.1 $\text{\AA}$.

ΔE^{2D} energy difference points slightly above the connecting line. This finding suggests a tendency for decomposition and segregation into pure Al or alloy M coverage and Al_2Zr_2 if kinetically accessible. Therefore, Fig. 3 also reflects the segregation tendencies of alloying elements on different aluminum crystal planes. Comparing the absolute values of the energy differences for different alloying atoms, the energy difference range for Mg covered surfaces relative to pure aluminum or pure Mg covered surfaces is between -0.34 eV and 0 . The surface concentration variation of Si has a minimal impact on surface stability. In contrast, Sc and Zr significantly enhance stability on these crystal faces, particularly at intermediate concentrations or specific surfaces. For example, the energy difference range for Zr can be as low as -1.66 eV, and the stabilizing effect of Sc on the (110) face results in an energy difference as low as -1.69 eV.

B. Differential electron density of surface alloys

To investigate the binding mechanism of the alloying elements Zr, Sc, Mg, Si in the most stable alloys on the Al (111) surface, the differential electron density $\Delta\rho$ was calculated for

structure models with complete surface coverage according to Eq. (5):

$$\Delta\rho = \rho_{\text{AlM}} - \rho_{\text{Al}} - \rho_M. \quad (5)$$

Here, ρ_{AlM} denotes the total charge density of the Al slab containing the alloying atom, ρ_{Al} is the charge density of the Al slab without the alloying atom, and ρ_M corresponds to the charge density of the isolated alloying atom at the same position where it is located in the alloy supercell. This approach visualizes the redistribution of electronic density upon alloying. The electron density scale in Fig. 4 was normalized according to Eq. (6):

$$\rho \propto \frac{N}{R_{\text{est}}^3}, \quad (6)$$

where ρ represents the estimated electron density, N denotes the effective number of inner electrons, and R_{est} corresponds to the estimated inner shell radius for each alloying element. For Zr, Sc, and Mg, the pseudopotential files account for both inner and valence electrons, enabling the effect of localized inner orbitals: $(4s^2, 4p^6)$, $(3s^2 3p^6)$, and $(2s^2 2p^6)$, respectively. The characteristic radii were estimated using

noble gas analogs: Kr (0.88 Å), Ar (0.71 Å), and Ne (0.38 Å) [38]. As evident in Figs. 4(c)–4(e), the observed spots exhibit dimensions consistent with the reference values.

Figure 4 displays cuts through the alloying atoms M segregated to the surface of the Al slab perpendicular to the Al (111) plane both through the alloying atoms as shown in Figs. 4(a) and 4(c)–4(f), and through bonds in-between as shown in Figs. 4(b) and 4(g)–4(i), which reflects the influence of the underlying Al layers more closely. The color scale represents $\Delta\rho$. The elements are arranged such that the nominal spatial extension of the valence electrons decreases [38] from left to right: of isotropic $4d$ - and $3d$ -type for Zr and Sc; isotropic, diffuse $3s$ -type for Mg; and pronouncedly directional $3p$ -type for Si. All three metal atoms—Zr, Sc, and Mg—are larger than the surrounding Al atom, but exhibit a radially polarizable electron density, which leads to a slight isotropic compression of the semicore states that is observed as mostly spherical electron accumulation in the cut through the M atoms and an electron depletion in the region in-between [Figs. 4(g)–4(i)]. For Zr and Sc, an electron accumulation at the Al atoms of the second layer with no pronounced directionality is obtained. For Mg, the underlying Al atoms are not noticeably affected. In contrast, for Si as a top layer, a rather complex electron redistribution pattern is obtained which exhibits distinct directionalities of the bonding to the Al slab.

For all investigated alloying atoms, we observe that upon incorporation into the Al matrix, the crystal field effect due to the surrounding atoms modifies the electron distribution; orbitals contract if one effectively increases their nuclear charge expanding the valence orbital dimensions. Subtraction of the density of the alloying atom layer leads to nearly spherical electron enrichment in the semicore region with a hole inside for the density of the core electrons included in the pseudopotential. Notably, the intrinsic semicore orbital sizes compare well with their noble gas counterparts due to the Al crystal field effects [red circles in Fig. 4(a)]. For Si, where the pseudopotential considers only valence electrons ($3s^2 3p^2$), we employed a scaling factor corresponding to $R_{\text{est}} = 1.11$ Å [38]. Figure 4(f) demonstrates similar field effects on these valence orbitals, indicating an expansion of the Si valence, which is similar to the case of the metals, but also hints towards a directional nature of the Si-Al bonding. The observed asymmetry arises from vacuum interface effects above the surface.

The analysis of the electron density differences in the interstitial regions [Figs. 4(b) and 4(g)–4(j)] reveals further valence electron redistribution. The spot sizes representing valence orbital cross-sections in Figs. 4(g)–4(i) correlate well with calculated atomic radii for Zr (2.06 Å), Sc (1.84 Å), and Mg (1.45 Å) [38]. The electron-deficient regions (blue) indicate charge transfer from the alloying layers to Al atoms, which correlates well with the electronegativity differences (electronegativity: Zr 1.33, Sc 1.36, Mg 1.31, Al 1.61) [39], particularly evident in Figs. 4(g) and 4(h). For Sc we observe an anisotropy of the redistributed electrons, which exhibits a distinctly d -type character; this finding aligns well with previous results in which, contrary to most $3d$ metals, the Sc^{2+} radical cation retains an electron with s -type symmetry

[40,41]. The Si case (electronegativity 1.90) exhibits more complex behavior of mutual valence electron shifts [Fig. 4(f)].

C. Surface alloy precipitation tendency

As illustrated in Fig. 5, the comparative analysis shows four substituted alloy structures of Al_2M_2 on Al(001) and Al(110) surfaces. For the Al(001) surface, there are two distinct configurations, and three surface structures exist. Before the structure optimization, the interatomic distances between alloy atoms were 4.05, 2.86, and 4.96 Å, respectively, across these configurations. On the Al(001) surface shown in Figs. 5(a)–5(d), the first studied structure of Al_2Mg_2 exhibited a more stable energy of -0.34 eV relative to -0.06 eV for the second structure. Similarly, Al_2Si_2 exhibited a preference for structure 1 with $\Delta E^{2D} = -0.19$ eV over structure 2 with -0.11 eV. Remarkable stabilization was observed for Al_2Zr_2 in the structure with the longer interatomic distance (-1.66 eV), exceeding the stabilization of the alloy with the shorter atomic distance (-0.33 eV). Al_2Sc_2 followed this trend with structure 1 showing a pronounced stability with ΔE^{2D} of -1.69 eV compared to structure 2 with -0.40 eV.

For the Al(110) surface shown in Figs. 5(e)–5(h), Al_2Mg_2 displayed comparable stability for the first structure with a relative stabilization by -0.24 eV and the third structure with -0.25 eV. The second structure with an interatomic distance of 2.86 Å between the alloy atoms exhibited positive ΔE^{2D} values, indicating a decomposition tendency. Al_2Si_2 configurations demonstrated minimal variations of the energy difference of approximately zero, suggesting negligible impact on the aluminum surface stability. Al_2Zr_2 shows moderate stabilization for both the first structure (-0.73 eV) and the third structure (-0.53 eV), contrasting with an unstable situation for structure 2 with a positive value of ΔE^{2D} (0.25 eV). Similarly, Al_2Sc_2 shows stabilization for the first (-0.94 eV) and third structure (-0.89 eV), while the nearest interatomic distance between Sc atoms remained unstable with a positive relative energy difference. A consistent trend is also shown for the surfaces Al(001) and Al(110). The configurations with alloy atom spacings of 4.05 Å demonstrated maximal stability, followed by 4.96 Å spacings in the third surface configuration, while 2.86 Å spacings consistently exhibited positive ΔE^{2D} values, indicative of surface decomposition tendencies.

Literature findings also indicate that the formation of Al_3Zr precipitates in aluminum alloys exhibits a thermodynamic advantage. The Al_3Zr precipitates typically have an $L1_2$ ordered structure, which is a face-centered-cubic structure where Zr atoms occupy the corner positions and Al atoms occupy the face-centered positions [42,43]. This ordered structure maintains a good coherency relationship with the aluminum matrix, which is beneficial for the stability and strengthening effect of the precipitation. For the 2D analog of the Al_3Zr precipitates, the energy lies on the convex hull, indicating a stable structure [44]. The interatomic distance between Zr atoms is 4.0 Å, which matches the alloy atomic spacing in structure 1 of the current study, which is energetically favorable. Hence, structure 1 may be considered as a precursor of the nucleation site for Al_3Zr precipitate formation.

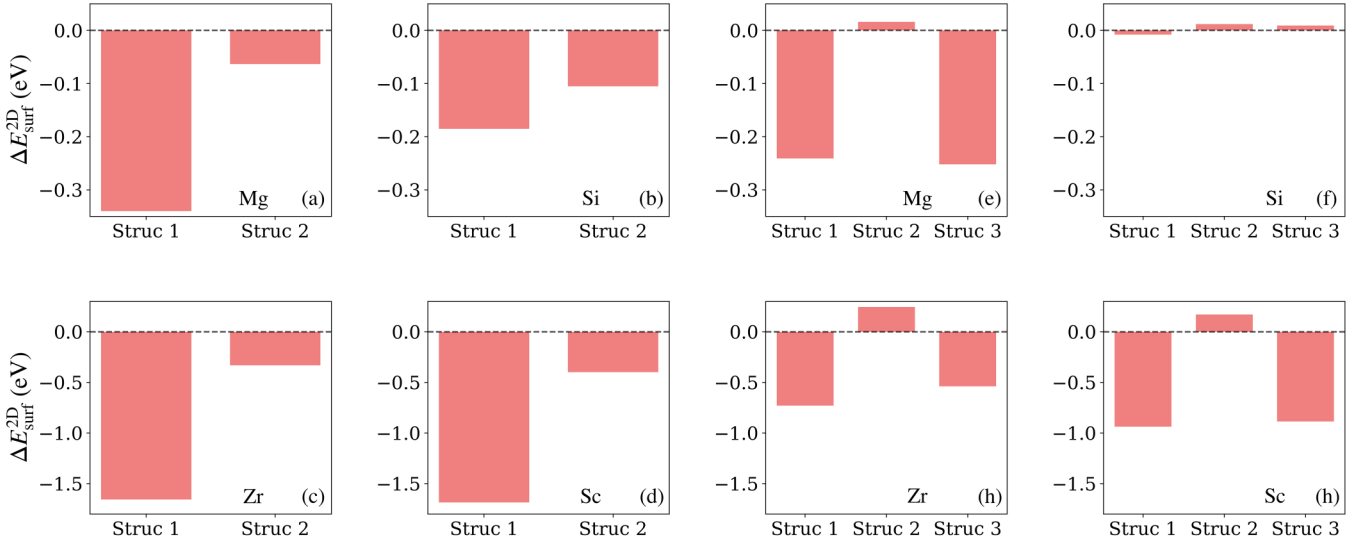


FIG. 5. The relationships between the surface alloy structures of Al_2M_2 and ΔE^{2D} for (a) Mg, (b) Si, (c) Zr, and (d) Sc on the aluminum (001) crystal plane, as well as for (e) Mg, (f) Si, (g) Zr, and (h) Sc on the aluminum (110) crystal plane.

D. Surface alloy diffusion

The study further investigated the diffusion tendency of alloying atoms to the aluminum (110), (111), and (001) surfaces from the bulk alloy. As the alloy atom moves from an inner-layer substitutional site towards substituting an aluminum atom on the surface, the energy difference associated with this diffusion process serves as an indicator of the atom's tendency to migrate to the surface and destabilize the bulk alloy. The calculation is shown in Eq. (7):

$$\Delta E_{\text{diffusion}} = E_{\text{total}}^{\text{upper layer}} - E_{\text{total}}^{\text{deepest diffusion layer}}. \quad (7)$$

The deepest diffusion layer corresponds to the fourth atomic layer, which is treated as the bulk reference due to its central position within the four fully relaxed surface layers of the slab structure. The first term on the right side represents the total energy of the slab when the alloying atom is positioned above the fourth layer. A negative $\Delta E_{\text{diffusion}}$ indicates that the alloying atom is more stable at the specified layer than in the reference layer, suggesting a preference for segregation toward the surface. Conversely, a positive value implies lower stability at the given layer compared to the reference layer, reflecting a driving force for diffusion into the bulk. So this energy difference quantitatively characterizes the tendency of alloying atoms to diffuse toward either the surface or the bulk.

Figure 6 compares the trends obtained for the different alloying atoms on the basis of the diffusion energies calculated for the three low-index surfaces. The Mg atom demonstrates a consistent preference across all three surfaces, with negative diffusion energies in the first layer of aluminum ranging from -0.23 to -0.41 eV. This indicates that Mg has a strong tendency to reside on the outermost surface of these three planes, as the surface positions are energetically more favorable compared to the interior bulk of aluminum. Additionally, the energy of Mg increases sharply from the first layer to the second layer for all three surfaces, indicating a strong surface segregation trend. Si atoms exhibit slightly negative energies in the surface layer of aluminum ranging from -0.04

to -0.23 eV, suggesting a weaker tendency for surface segregation compared to Mg.

In contrast, the transition metal elements Zr and Sc show significantly positive energy differences in the outermost layer of the three aluminum surfaces. Specifically, the diffusion energy difference for Zr atoms ranges from 0.37 to 0.91 eV, while for Sc atoms it ranges from 0.12 to 0.36 eV. This indicates that Zr and Sc tend to avoid the outermost surface of the aluminum crystal, as the surface positions are energetically unfavorable compared to the bulk interior. Moreover, Zr has a stronger tendency to diffuse into the bulk of aluminum than Sc. The energy of Zr and Sc decreases sharply from the first layer to the second layer on the same surface, further indicating that they are relatively stable in the subsurface or deeper layers.

Furthermore, Fig. 6 also reveals the influence of the surface orientation of aluminum. Although the qualitative trends of the alloying atoms are similar across the three surfaces, the specific energy values differ. Mg exhibits the strongest segregation driving force to the (110) surface with -0.41 eV, compared with the (111) and (001) surfaces. Zr and Sc show the highest positive energy values on the (110) surface in the top first layer indicating the strongest diffusion trend away from this surface. This is related to the surface formation of pure aluminum, where the (111) surface has the lowest surface energy and is the most stable surface for aluminum, compared with the (001) and (110) surfaces.

Experimental data show that the concentration of Mg on the Al surfaces increases with increasing environmental temperature [45]. This indicates that Mg has a tendency to diffuse to the aluminum surface. This observation aligns well with the computational results of the current study. The diffusion coefficient of Si in aluminum is higher than that of Al [46], resulting in faster diffusion of Si compared to Al. Together with the calculated propensity of Si atoms for a position in the Al surface layer, this finding suggests that Si segregates to the Al surface in the pure Al-Si diffusion couple. Si forms stable 2D surface phases on the dense (001) and (111) surfaces,

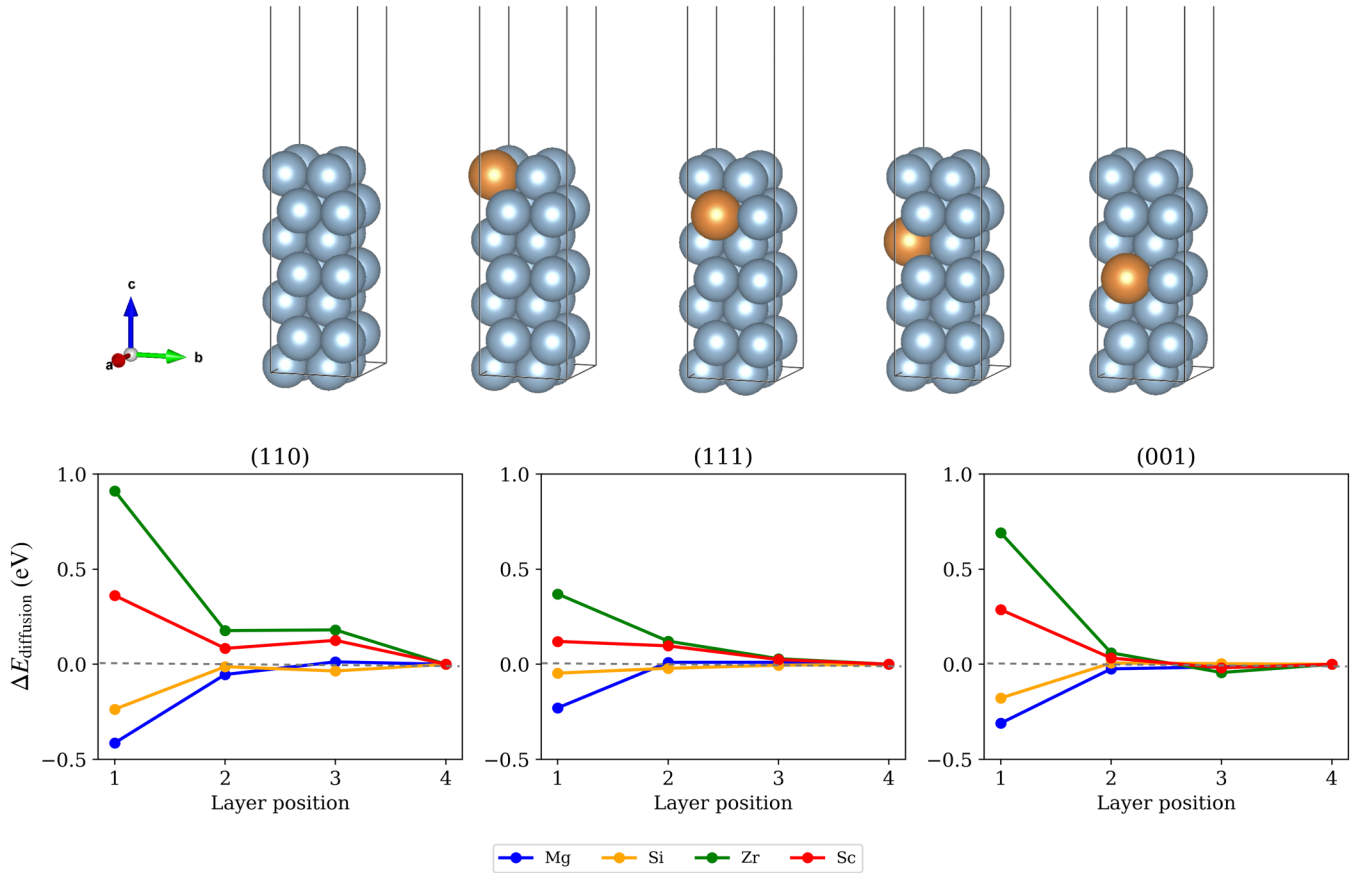


FIG. 6. (a) Schematic illustration of the diffusion of alloying atoms on the aluminum (001) crystal plane. Energy differences for the diffusion of one alloying atom towards the aluminum crystal planes (b) (001), (c) (110), and (d) (111).

which have no equivalent 3D bulk phase; the less dense and anisotropic (110) surface does not support 2D surface phase formation with Si. Conversely, the diffusion coefficient of Zr is three orders of magnitude lower than that of Al [47], leading to slower diffusion of Zr relative to Al and classical 3D precipitate formation in the bulk alloy.

E. Differential electron density toward the surface

To understand the diffusion behavior of alloying atoms within the Al slab, vertical cross-sections of the electron density difference along the directions indicated in Figs. 7(a)–7(d) are analyzed. We compare Si (middle row) and Zr (bottom row), because they exhibit very different trends regarding segregation and 2D surface phase formation in the previous sections. The density difference associated with the Si top layer exhibits a rather directional pattern, which reaches further into the bulk and is much more complex than the predominantly isotropic patterns obtained for the surface layers of the metals Mg, Sc, and Zr. Therefore, for studying the influence of the electronic structure on the diffusion behavior, we may compare the electron density difference plot for Si with any of the three other metallic alloying elements. We choose Zr, because Si is formally isovalent (Si: $3s^2, 3p^2$; Zr: $5s^2 4d^2$) with one valence electron more than the atoms of the surrounding Al matrix, but it features different angular momentum characteristics. Figure 7 compares the electron

density redistribution at the different substitutional sites along the diffusion path for Si and Zr, starting with the position in the top layer to the second, third, and fourth layers from left to right for the case of Al(111).

Overall, Zr and Si exhibit different differential charge density features within the Al lattice. As the alloying atom migrates from the interior to the outermost surface of the Al slab, the differential charge density changes, especially when the atom reaches the surface layer. In this case, the vacuum-facing side transitions from electron accumulation to electron depletion, a behavior observed for both Si and Zr. In contrast, when the alloying atom resides in subsurface layers (e.g., second to fourth layer), the surrounding differential charge density is more isotropic along the surface normal and nearly independent of the depth beneath the surface layer for both alloy atoms. The key influencing factors for the differences between Si and Zr include valence electron configuration, orbital symmetry, and spatial extent, as well as the nature of the alloy-Al bonding and surface coordination. The ground-state configuration of Si is $[\text{Ne}]3s^2 3p^2$, with directional $3p$ (p_x, p_y) valence electrons. As depicted in Figs. 7(e)–7(h), the $3p$ orbitals possess lobes oriented in-plane or perpendicular to the (111) direction. On vertical cross-sections, this results in a characteristic “ring” of positive $\Delta\rho$ where the p -lobes overlap with neighboring Al atoms. As the directionality of the p -orbitals matches the surrounding cubic crystal field, relocating Si from the second to the fourth layer induces

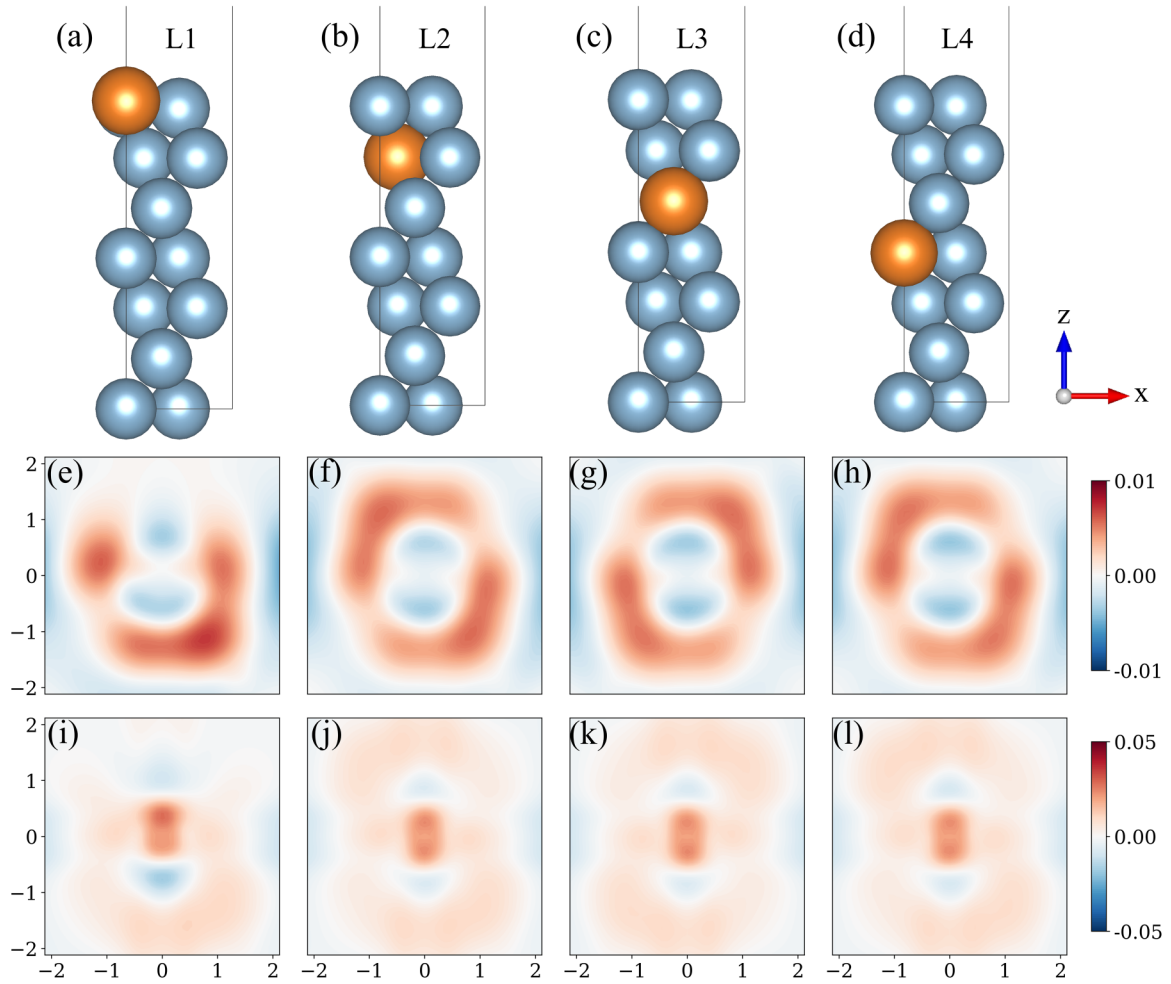


FIG. 7. The alloying elements Si and Zr, denoted as (M) and represented by golden spheres, substitute aluminum atoms in the Al(111) slab. Specifically, alloy atoms M replace Al atoms located at the (a) first, (b) second, (c) third, and (d) fourth atomic layer of the slab. Cuts through the electron density difference in the (x, z) plane are depicted for the cases where the Si atom substitutes the Al atom at the (e) first, (f) second, (g) third, and (h) fourth layer of the Al(111) slab; the Zr atom substitutes the Al atom at the (i) first, (j) second, (k) third, and (l) fourth layer. All density difference plots depict an area of $2.1 \text{ \AA}$ by $2.1 \text{ \AA}$.

minimal changes in the differential charge density, because the local geometric environment remains largely unchanged. Zr has a ground-state valence configuration of $[\text{Kr}]4d^2 5s^2$ and explicitly treated $4s^2 4p^6$ semicore states. As shown in Figs. 7(i)–7(l), Zr possesses partially filled $4d$ shells, resulting in complex bonding patterns elongated in the z direction. Along the (111) vertical section, d_{z^2} lobes align with the surface normal, while $d_{xy}/d_{x^2-y^2}$ lobes lie in-plane, generating quadrupolar red-blue-red features in the differential density maps. The pattern arises from valence shell structures and reflects the low electronegativity of Zr in comparison with Al.

IV. CONCLUSION

This study used density functional theory to investigate the stability and diffusion tendency of alloy atoms Mg, Si, Zr, and Sc on and towards the (001), (110), and (111) crystal surfaces of aluminum. The surface stabilities were most pronounced when the alloy atoms Mg, Si, Zr, and Sc constituted 50% of the surface composition. On the (111) surface,

the relationship between surface alloy composition and the surface stability energy difference formed a convex hull. The surface alloy phases formed by Sc and Zr with aluminum demonstrated significantly higher stability compared to their pure element counterparts, whereas the surface alloy phases formed by Mg and Si exhibited a relatively lower influence on the surface stability. Si had a minimal impact on the stability of these surfaces. For identical surface alloy compositions with different configurations, alloy atom spacings of $4.05 \text{ \AA}$ demonstrated maximal stability, followed by $4.96 \text{ \AA}$ spacings which are common in binary Al: M compounds. At a spacing of $2.86 \text{ \AA}$, the 2D alloy formation energy indicates a tendency towards surface decomposition. Additionally, Mg, Si, Zr, and Sc exhibited varying diffusion tendencies from the aluminum bulk to the aluminum surfaces. Mg and Si tended to segregate towards the surface, with Mg having a stronger driving force. In contrast, Zr and Sc tended to deplete from the surface, with Zr showing a weaker surface diffusion tendency towards the outmost surface of aluminum compared to Sc. The analysis of the electron density redistribution patterns in the contact regions between the Al matrix and

the alloying atoms indicated that the observed anisotropies reflected the spatial characteristics of the involved orbitals. Thus, despite very similar values of formal descriptors such as the ionic radii or the electronegativity, the specific electronic state of the alloying atom determined its effect on the bulk and surface properties of the aluminum alloy. In summary, the observed differences between Mg, Sc, Zr, or Si alloying atoms in an Al matrix stem from the specific electronic structure of the alloying atoms, which determines the binding geometry and its directionality in addition to the atom size, its polarizability, and its propensity to accept or release electrons.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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