



Article

First-Principles Study of Rare-Earth Doping Effects on Nitrogen Adsorption and Diffusion in Chromium

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Abstract

To address the premature corrosion failure of chromium-based coatings in harsh environments (e.g., high temperatures, chloride-containing solutions), this work systematically investigates how rare-earth (RE, i.e., Ce and La) elements regulate nitrogen (N) adsorption and diffusion behavior in Cr during the early stages of nitriding, a critical corrosion protection strategy, using first-principles density functional theory (DFT). Results show that RE preferentially occupies Cr substitutional site, increasing the Young's modulus from 293.5 GPa (pristine Cr) to 344.9 GPa (Ce-doped) and 348.7 GPa (La-doped). Surface RE doping on Cr(110) significantly enhances N adsorption energy from -3.23 eV to $-3.559/-3.645$ eV (Ce-/La-doped), whereas subsurface doping slightly weakens the adsorption. Moreover, the energy barrier for N penetration into subsurface is reduced from 2.11 eV to 2.03/1.91 eV (Ce-/La-doped), thereby facilitating nitridation. Notably, RE is found to strongly trap vacancies and N atoms, leading to increased migration barriers and thus hindering their long-range transport. These findings demonstrate that RE exhibits a dual role during nitriding: promoting N incorporation at the surface while restricting its deep diffusion into the bulk. The study provides theoretical insights into the atomistic mechanisms by which RE elements modulate nitriding efficiency in Cr-based alloys, offering guidance for the design of RE-doped surface-modified coatings with improved corrosion resistance.

Keywords: chromium-based materials; nitridation; corrosion protection; rare earth doping; density functional theory



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1. Introduction

Austenitic stainless steels are extensively used in various industrial fields due to their excellent corrosion resistance and toughness [1,2]. However, limitations such as low surface hardness, inadequate wear resistance, and susceptibility to pitting significantly restrict their performance under harsh environments [3,4]. Nitriding is recognized as an effective surface modification technique, as it substantially enhances wear and corrosion resistance by forming hard, nitrogen-rich Cr_xN phases on the surface [5–7]. Chromium (Cr) is frequently utilized as an alloying element or coating material, as it readily forms dense

Cr_xN layers during nitriding, thus imparting superior surface properties to stainless steels. Consequently, understanding nitrogen diffusion behavior in Cr and related structures during nitriding is critical for optimizing the quality and properties of these coatings.

The diffusion of nitrogen atoms is inherently influenced by intrinsic lattice characteristics and various defect states, including vacancies and dislocations. Recently, rare earth (RE) elements have been widely employed in thermochemical treatments such as nitriding and carburizing to enhance diffusion rates and coating quality due to their unique electronic structures and atomic-scale alloying behaviors [8,9]. Experimental investigations have indicated that RE elements catalyze the nitriding process primarily through the following mechanisms [10,11]: (1) promoting the decomposition of nitriding media and increasing active nitrogen concentrations; (2) strengthening nitrogen adsorption capability at the surface, thereby elevating surface nitrogen potential; and (3) inducing lattice distortion and generating additional defects, thus creating more diffusion pathways. For instance, Zhao et al. [12] revealed that the addition of Ce and La to Q235 steel significantly improved the toughness and adhesion of the nitrided layer, which was attributed to rare earth diffusion into the compound layer and the enhancement of compressive residual stress. Zhang et al. [13] demonstrated that La addition during plasma nitriding of M50NiL steel accelerated nitrogen dissociation and promoted surface oxidation, thereby influencing nitrogen distribution and transport. Lazhar et al. [14] reported that Ce and La doping into 32CrMoNiV5 steel increased nitrogen diffusion rates, surface hardness, and nitrogen concentration gradients, indicating their catalytic roles in promoting nitriding kinetics. Furthermore, Li et al. [15] showed that lanthanum and yttrium ion implantation into 20Cr2Ni4A steel formed rare earth solid solutions and high dislocation densities, which enhanced the diffusion coefficient of carbon and improved the uniformity and hardness of the carburized layer. However, current understandings of these mechanisms are mainly based on studies of Fe-based systems, with limited insights into the effects of RE doping on nitrogen diffusion behavior in Cr-based systems.

First-principles calculations based on density functional theory (DFT) have proven to be an effective method for exploring the atomistic mechanisms of interstitial element transport in metallic systems. Yang et al. [16] investigated nitrogen adsorption and penetration behaviors on Fe surfaces with and without La/Ce doping and found that RE atoms at the surface significantly reduce nitrogen adsorption energies and stabilize the interfacial configuration, promoting nitrogen uptake. Sarita et al. [17] conducted a comprehensive study on the interaction of light interstitial solutes (C, N, B, O) with point defects in body-centered cubic (bcc) and face-centered cubic (fcc) Fe lattices, highlighting the strong binding between nitrogen and vacancies, especially in bcc structures. Yeo et al. [18] further decomposed the complete nitriding mechanism into elementary steps—adsorption, dissociation, penetration, and diffusion—on Fe surfaces, revealing that nitrogen penetration into the subsurface region exhibits the highest energy barrier and serves as the rate-determining step. These studies demonstrate the utility of DFT in quantitatively evaluating nitrogen–metal interactions and reveal how solute elements, local lattice distortions, and diffusion barriers collectively shape the nitriding process at the atomic level. However, most of these computational insights have been limited to Fe-based systems. Systematic investigations into Cr-based systems, particularly regarding the roles of different RE elements such as Ce and La, remain scarce. The impact of RE doping on defect energetics, nitrogen transport, and surface stability in Cr is thus still unclear and requires further theoretical clarification.

Therefore, this study systematically investigates the effects of Ce/La doping at substitutional sites in bulk and surface Cr on nitrogen atom adsorption and diffusion behaviors. By constructing RE-doped Cr surface models, we simulate nitrogen penetration from surface to subsurface regions, clarifying the impact of RE doping positions (surface or

subsurface, with the former denoting replacement of an outermost Cr atom and the latter denoting that a second-layer Cr atom of the of Cr(110) facet) on nitrogen adsorption capacities and diffusion barriers. Additionally, through analyses of vacancy formation energies and Cr self-diffusion behavior, we further elucidate how interactions between RE atoms and defects affect diffusion pathway evolution. The aim of this work is to provide atomistic-level theoretical insights into the catalytic mechanisms of RE elements on diffusion behavior in Cr, thus offering theoretical support and design guidelines for optimizing Cr-based surface nitriding processes.

2. Calculation Details

All first-principles calculations were carried out based on density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) [19]. The interactions between ions and electrons were described using the projector augmented wave (PAW) method [20], and the exchange-correlation energy was treated within the generalized gradient approximation (GGA) formulated by Perdew-Burke-Ernzerhof (PBE) [21]. A plane-wave cutoff energy of 500 eV was employed throughout. The electronic self-consistent convergence criterion was set to 10^{-6} eV, and atomic relaxations were performed until the Hellmann-Feynman forces on each atom were less than 0.01 eV/Å. Brillouin zone integrations were performed using a $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh for all supercells.

Because Cr crystallizes in the body-centered cubic (bcc) structure under ambient conditions [22], we modeled bulk Cr using a $3 \times 3 \times 3$ bcc supercell (54 atoms). The optimized lattice parameter calculated as 2.845 Å, consistent with experimental and theoretical values [23]. The doping behavior of RE atoms (Ce, La) was evaluated by modeling their occupancy at substitutional (S), octahedral (O), and tetrahedral (T) positions, as illustrated in Figure 1b–d. To quantify the energetic stability of these doped configurations, the solvation energy (E_{sol}) of RE atoms in Cr was calculated. For interstitial configurations (RE at O or T site), the solvation energy is computed as [24]:

$$E_{\text{bulk}}^{\text{inter}} = E_{\text{bulk}}^{\text{inter+RE}} - E_{\text{bulk}} - E_{\text{RE}} \quad (1)$$

For substitutional configurations (RE replacing a Cr atom), the solvation energy is calculated by:

$$E_{\text{sol}}^{\text{sub}} = E_{\text{bulk}}^{\text{sub+RE}} - \frac{n-1}{n} E_{\text{bulk}} - E_{\text{RE}} \quad (2)$$

In this case, $E_{\text{bulk}}^{\text{inter+RE}}$ and $E_{\text{bulk}}^{\text{sub+RE}}$ denote the total energies of the RE-doped supercells at interstitial and substitutional sites, respectively; E_{bulk} is the reference energy of the pristine Cr supercell, n is the total number of atoms in the supercell, and E_{RE} is the energy of the isolated RE atom. The computed solvation energy reflects the thermodynamic stability of the RE-doped configurations. Higher solvation energies indicate less stable configurations, whether the RE atom resides in the substitutional, octahedral, or tetrahedral site.

To examine the interaction strength between RE atoms and vacancies, the binding energy (E_b) between RE and vacancy was calculated using the following expression [17]:

$$E_b(\text{RE} + \text{V}) = E(\text{RE}) - E(\text{V}) - E(\text{RE} + \text{V}) - E_{\text{ref}} \quad (3)$$

where $E(\text{RE})$ and $E(\text{V})$ are the total energies of supercells containing only the RE atom and only the vacancy, respectively; $E(\text{RE} + \text{V})$ is the total energy of the supercell with both the RE atom and vacancy present; and E_{ref} is the energy of the pristine Cr supercell. A positive binding energy indicates an attractive interaction between RE and vacancy.

Surface calculations were conducted on the Cr(110) slab constructed from a 2×2 surface unit cell with six atomic layers. The bottom two layers were fixed during relaxation,

and a vacuum layer of 15 Å was introduced to avoid interactions between periodic images. A $6 \times 4 \times 1$ Monkhorst-Pack k-point mesh was used for slab calculations. The nitrogen adsorption energy (E_{ad}) on the surface was defined as [25]:

$$E_{ad} = E(Cr_{slab+N}) - E(Cr_{slab}) - E(N) \quad (4)$$

$E(Cr_{slab+N})$ is the total energy of the slab with an adsorbed nitrogen atom, $E(Cr_{slab})$ is the energy of the clean slab, and $E(N)$ is the energy of an isolated nitrogen atom in its ground state. A more negative adsorption energy indicates stronger adsorption.

The energy barriers for nitrogen diffusion from surface to subsurface, as well as vacancy-assisted diffusion of Cr atoms in bulk, were determined using the climbing-image nudged elastic band (CI-NEB) method [26].

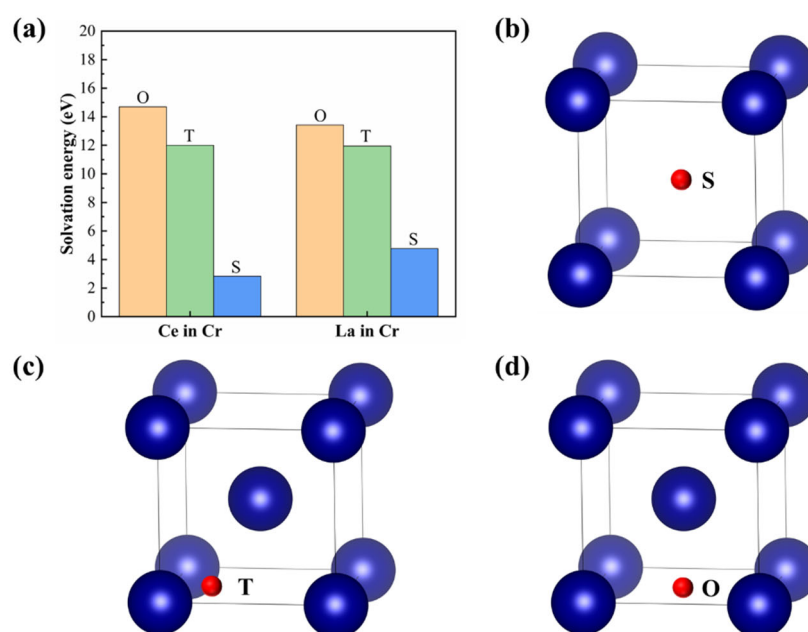


Figure 1. Calculated solvation energies of RE atoms (Ce and La) in Cr bulk. (a) Comparison of solvation energies at different lattice sites; atomic configurations for (b) S, (c) T, and (d) O sites, respectively. Blue spheres represent Cr atoms, and red spheres represent RE atoms.

3. Results and Discussion

3.1. Bulk Properties of Cr Doped with RE

To determine the energetically favorable doping configurations of RE atoms in bulk Cr, the solvation energies of RE atoms occupying S, O, and T sites were systematically calculated, as shown in Figure 1. Significant differences in solvation energies were observed for RE atoms depending on the occupied lattice sites. Specifically, the solvation energy of the S site is significantly lower compared to the solvation energies of the interstitial sites (O and T), which are more than 12 eV, indicating a highly unstable conformation. Such results explicitly suggest that RE atoms preferentially substitute Cr atoms rather than occupying interstitial lattice positions. The observed substitutional stability aligns well with general trends noted in metallic lattices, where larger dopant atoms preferentially substitute host lattice atoms to minimize lattice distortion and associated strain energy. Given the atomic radii of La (187 pm) and Ce (183 pm), significantly larger than that of Cr (128 pm), the preference for substitutional incorporation in the Cr lattice is further supported.

Additionally, to assess the influence of substitutional RE doping on the mechanical properties of Cr, the elastic constants (C_{11} , C_{12} and C_{44}) and associated mechanical parameters (bulk modulus B , shear modulus G , and Young's modulus E) were computed

for pristine Cr and RE-doped Cr, as presented in Table 1. The calculated lattice constant a_0 and elastic constants of Cr are in good agreement with previous first-principles results. By contrast, the calculated B and other elastic constants (C_{11} , C_{12}) are larger than the low-temperature experimental measurements. This systematic offset is expected because those experiments were performed on the incommensurate spin-density-wave (SDW) antiferromagnetic state of bcc-Cr with wave vector $2\pi/a$ (0.952,0,0) [27]. Magnetic ordering in Cr entails a slightly larger equilibrium volume and a softer elastic response than the magnetic state typically assumed in standard DFT. Rare earth element substitution can significantly improve the elastic stiffness of Cr. Specifically, Ce and La substitutions moderately enhance C_{11} and C_{44} , while significantly altering C_{12} , reflecting an improvement in both stiffness and shear resistance of the crystal. Quantitatively, the Young's modulus (E) notably increases from 293.5 GPa in pristine Cr to approximately 344.87 GPa and 348.72 GPa upon Ce and La doping, respectively. This improvement is attributed primarily to lattice distortion effects introduced by the substitutional RE atoms, enhancing the rigidity of atomic bonding within the Cr matrix. Such strengthening is expected to confer improved resistance against mechanical deformation, potentially beneficial in subsequent nitriding treatments.

These findings collectively illustrate that RE atoms preferentially occupy substitutional Cr sites, introducing minimal lattice distortion while significantly enhancing the intrinsic mechanical properties of the Cr matrix, thereby laying a robust foundation for subsequent discussions of RE influence on nitrogen diffusion mechanisms.

Table 1. The theoretical and experimental lattice constant (a_0), elastic constants (C_{11} , C_{12} , C_{44}), bulk modulus (B), shear modulus (G), and Young's modulus (E) of bcc Cr and RE-doped CrRE systems.

Type	$a_0/\text{\AA}$	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa	B/GPa	G/GPa	E/GPa
Cr	2.85	483.78	146.64	84.73	258.82	111.94	293.50
Cr _{calc} [28]	2.85	484	140	105	255	-	-
Cr _{exp} ^{77K} [27]	2.88	391.00	91.00	103.00	191.00	-	-
Cr ₅₃ Ce	2.86	510.34	139.15	108.29	262.88	134.57	344.87
Cr ₅₃ La	2.86	508.86	139.85	111.16	262.85	136.34	348.72

3.2. Adsorption Properties of Nitrogen Atom on Cr(110)

To elucidate the interactions between nitrogen atoms and rare-earth (RE)-doped Cr surfaces, adsorption behaviors on pristine and RE-doped (RE = La, Ce) Cr(110) surfaces were systematically investigated. The Cr(110) surface was selected for analysis due to its densely packed atomic arrangement and its thermodynamic stability, making it the most commonly exposed surface in polycrystalline Cr-based materials under nitriding conditions. This surface orientation is thus of particular relevance in practical surface treatment applications. Initially, nitrogen adsorption energies at various adsorption sites on the pristine Cr(110) surface were computed, with the results summarized in Table 2. The calculations reveal that nitrogen atoms preferentially adsorb at the high-coordination long-bridge (LB) site, which exhibits the most negative adsorption energy, indicating the strongest adsorption capability. For pristine Cr(110), there is a clear negative correlation between the distance of the nitrogen atom from the surface (h_{N-S}) and the magnitude of the adsorption energy: nitrogen atoms located closer to the surface exhibit more negative adsorption energies. This trend reflects stronger metal-nitrogen bonding interactions at shorter bonding distances, as evident from the numerical data in Table 2. Such a relationship is consistent with classical adsorption principles and further confirms the LB site as the most favorable configuration for nitrogen on Cr(110). Upon rare earth doping, changes in coordination and local distortion/electronic structure disrupt this monotonic relationship; therefore, the adsorption energy does not scale simply with h_{N-S} across different sites and dopant configurations.

Subsequently, the adsorption properties on RE-doped Cr surfaces, specifically those with RE substitutions in either the surface (Cr_{RE}^{surf}) or subsurface (Cr_{RE}^{sub}) layers, were comparatively analyzed. The LB sites remain energetically favored on both pristine and RE-doped surfaces, suggesting minimal influence of subsurface RE doping on adsorption site preference. As shown in Table 2, nitrogen adsorption is more exothermic on surface-layer RE doping (Cr_{La}^{surf} and Cr_{Ce}^{surf}) compared to the pristine surface, while subsurface doping (Cr_{La}^{sub} and Cr_{Ce}^{sub}) slightly less exothermic adsorption than Cr_{RE}^{surf} . Additionally, structural relaxation results reveal notable positional shifts in RE atoms following surface doping. Due to their larger atomic radii, Ce atoms in the surface-doped configurations are displaced outward toward vacuum by approximately 1.131 Å, compared to only 0.161 Å for subsurface-doped configurations (as indicated by arrows in Figure 2). Upon nitrogen adsorption, Ce atoms experience further inward shifts by 0.742 Å and 0.017 Å, respectively, highlighting strong Ce-N bonding interactions at the surface layer. The subsurface doping, by expanding the interlayer spacing, weakens the direct interactions between nitrogen atoms and subsurface atoms, thereby diminishing nitrogen adsorption strength. To gain deeper insights into the electronic origins underpinning these adsorption trends, the projected density of states (PDOS) for nitrogen adsorbed on Ce-doped Cr(110) at optimal adsorption configurations were analyzed. The h_{N-S} value at the LB1 site on Cr(110) is an outlier and does not follow the inverse relation between h_{N-S} and E_{ads} . As illustrated in Figure 3, the Ce d-band center at the LB1 site in Cr_{RE}^{surf} lies farther from the Fermi level than at the LB2 site. According to d-band theory, a d-band center closer to the Fermi level typically indicates stronger hybridization between metal d-orbitals and adsorbate states, thus enhancing adsorption strength. The nitrogen atom on Cr_{RE}^{surf} is coordinated to three Cr atoms and one Ce atom, whereas on Cr_{RE}^{sub} it is coordinated to four Cr atoms. Relative to subsurface doping, the surface-layer Ce exhibits a stronger N-RE interaction; hence, the subsurface-doped case shows weaker adsorption.

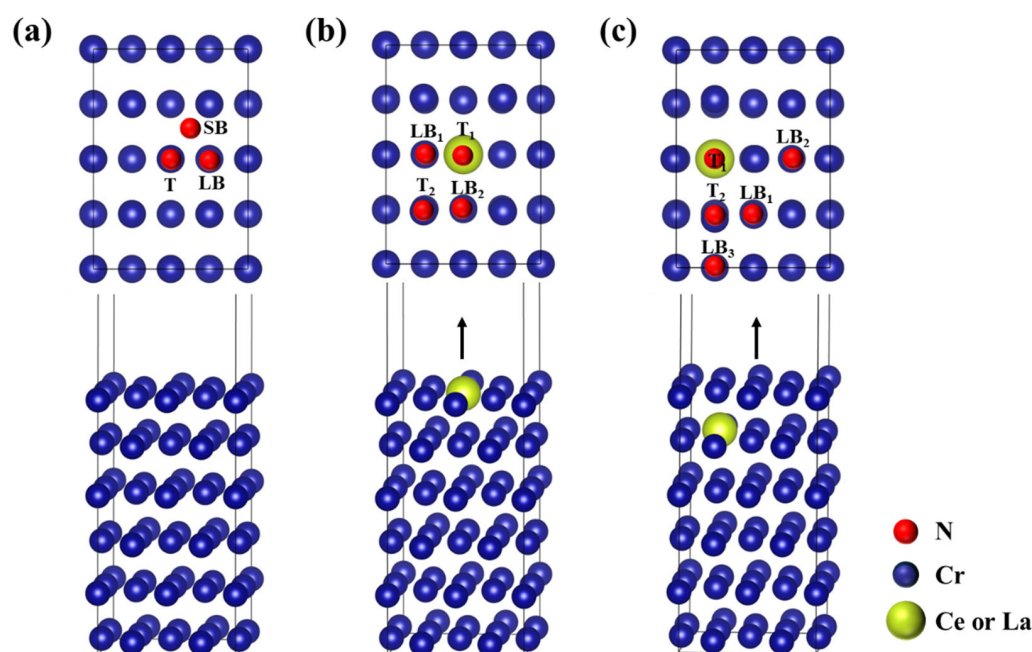
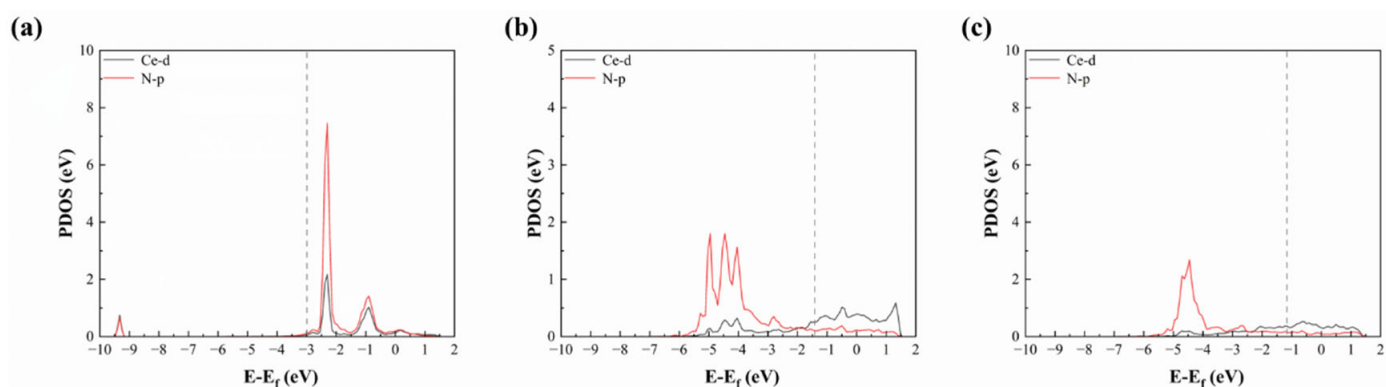


Figure 2. The nitrogen atom adsorption on (a) Cr(110) surface with the RE atom doped (b) $Cr_{RE}^{surf}(110)$; (c) $Cr_{RE}^{sub}(110)$. Upper and lower part of (a–c) denote respectively top-view and side-view. T represents on-top site, LB represents long bridge site, SB represents short bridge site. Arrows in (b,c) mean an outward displacement of the RE atom doped at the surface or subsurface.

Table 2. Equilibrium distances and absorption energies (E_{ad}) of nitrogen atoms on Cr(110), Cr_{RE}^{surf} (110) and Cr_{RE}^{sub} (110).

	Initial Site	E_{ad} (eV/Atom)	h_{N-S} (Å)	Final Site
Cr(110)	T	−0.921	1.604	T
	LB	−3.230	1.027	LB
	SB	−2.490	1.207	SB
Cr_{Ce}^{surf} (110)	T1	1.285	1.753	T1
	T2	−3.559	1.100	LB2
	LB1	−2.597	0.924	LB1
	LB2	−3.559	1.100	LB2
Cr_{Ce}^{sub} (110)	T1	−3.021	0.755	T1
	T2	−3.448	0.842	LB3
	LB1	−3.226	1.036	LB1
	LB2	−2.881	1.074	LB2
	LB3	−3.448	0.842	LB3
Cr_{La}^{surf} (110)	T1	2.151	4.296	T1
	T2	−3.645	1.117	LB2
	LB1	−3.177	0.765	LB1
	LB2	−3.645	1.117	LB2
Cr_{La}^{sub} (110)	T1	−3.333	1.106	T1
	T2	−3.440	0.983	LB3
	LB1	−3.248	1.053	LB1
	LB2	−2.999	0.738	LB2
	LB3	−3.440	0.983	LB3

Final site: the site occupied by the adsorbate after full geometry optimization.

**Figure 3.** The partial density of states (PDOS) for nitrogen adsorbed on Cr_{Ce}^{surf} (110) at the (a) T, (b) LB1 and (c) LB2 sites.

These computational insights confirm the essential role of surface-layer RE doping in enhancing nitrogen adsorption capability on Cr surfaces. This enhanced adsorption capacity is critical for increasing surface nitrogen concentration, potentially facilitating subsequent nitriding reactions and the formation of nitrided surface layers with improved mechanical properties.

3.3. Penetration Mechanism for Nitrogen Atom with RE Doping

To elucidate how RE doping modifies nitrogen penetration from the Cr(110) surface into the subsurface during the early stage of nitriding, we computed the minimum-energy path using the CI-NEB method. The diffusion path was defined as the migration of a nitrogen atom from the most favorable surface LB2 adsorption site to the nearest subsurface octahedral interstitial site. As indicated in Tables 2 and 3, the LB2 site exhibits the lowest

adsorption energy among the possible configurations, while the small atomic radius of nitrogen makes the octahedral interstitial site the most likely diffusion destination beneath the surface.

As shown in Figure 4, the energy barrier for nitrogen penetration into pristine Cr(110) is calculated to be 2.11 eV, which reflects the dense atomic packing and intrinsic diffusion resistance of the bcc Cr lattice. Upon substitution of surface Cr atoms with RE elements, the energy barrier is slightly reduced to 2.03 eV for Ce doping and to 1.91 eV for La doping. Although the reduction is moderate, the trend is consistent with the enhanced nitrogen adsorption observed in Section 3.2, suggesting that RE doping at the surface primarily influences the adsorption stage of nitrogen rather than drastically altering the migration barrier. The improvement in surface nitrogen affinity due to La and Ce doping may contribute to a lower overall energy requirement for the initial nitrogen uptake, thereby facilitating the onset of nitriding. Similar findings have been reported in previous experimental studies, which showed that RE atoms refine grain size and introduce lattice distortion, thereby providing more diffusion channels for nitrogen atoms. Furthermore, when the effect of RE doping on diffusion outweighs its effect on adsorption, nitrogen accumulation at the surface may be reduced, potentially suppressing nitride formation and leading to a steady-state thickness of the compound layer [12].

Table 3. Adsorption energies (E_{ad}) of nitrogen atom in Cr subsurface layer at different sites.

	Cr(110)		Cr_{Ce}^{surf} (110)		Cr_{La}^{surf} (110)	
Site	O	T	O	T	O	T
E_{ad} (eV/atom)	−1.697	−0.352	−2.035	−0.909	−2.095	−0.584

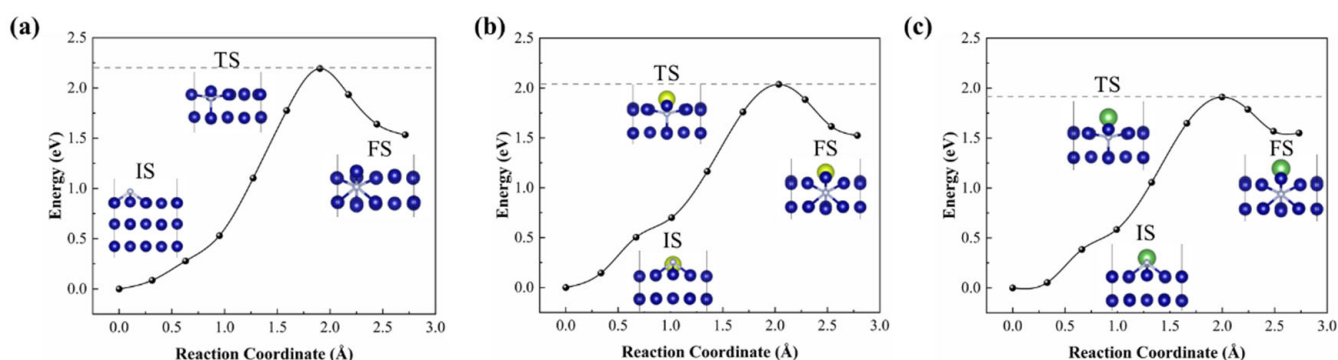


Figure 4. Minimum energy paths of nitrogen penetration into Cr(110), Cr_{Ce}^{surf} (110) and Cr_{La}^{surf} (110). The dashed line represents the energy barrier of nitrogen penetration into Cr(110). The gray balls represent nitrogen atoms, the blue balls represent chromium atoms in (a), and the yellow balls in (b) and the green balls in (c) represent Ce and La atoms, respectively.

3.4. Influence of RE Doping on Nitrogen and Vacancy Diffusion Behavior in Bulk Cr

To further understand the influence of RE doping on nitrogen transport beyond surface adsorption and penetration, we extended our investigation to the bulk Cr lattice, focusing on how Ce and La substitutions affect vacancy-mediated Cr self-diffusion and nitrogen interstitial diffusion. Both processes are critical for controlling nitrogen uptake depth and microstructural evolution during the nitriding of chromized layers.

As shown in Figure 5, the formation energy of a single Cr vacancy in undoped bcc Cr is calculated to be 2.688 eV, indicating that the spontaneous formation of vacancies is energetically unfavorable. Upon RE doping, however, the vacancy formation energy is significantly reduced, particularly when the vacancy is located in close proximity to the RE atom. For instance, when the vacancy resides at the nearest-neighbor site to

Ce, the formation energy drops to 0.836 eV; for La, an even lower value of 0.287 eV is observed. As the distance between the vacancy and RE atom increases, the formation energy gradually recovers toward the value of undoped Cr, implying a strong short-range interaction between RE atoms and vacancies. To further quantify the interaction between RE atoms and vacancies, the RE-vacancy binding energies were calculated at various distances. As shown in Figure 5b, the binding energy between a Ce atom and a Cr vacancy reaches 1.853 eV when they are nearest neighbors, while the corresponding value for La is 2.401 eV. A positive binding energy indicates a thermodynamically favorable attractive interaction between the RE atom and the vacancy, suggesting that RE dopants energetically promote vacancy trapping. As the distance between the RE atom and the vacancy increases, the binding energy gradually decreases, even becoming negative in some configurations (for instance, reaching -0.064 eV for Ce and -0.077 eV for La) indicating repulsive interactions at longer range. This distance-dependent trend highlights the strong short-range attraction and negligible or unfavorable long-range interaction between RE atoms and vacancies. Such behavior is consistent with previous findings in Fe-based systems, where oversized solute atoms (e.g., La, Ce) relieve local lattice strain in the vicinity of vacancies and form energetically stable vacancy-solute pairs. The pronounced short-range attraction implies that RE atoms can effectively trap vacancies within their local coordination environment, which may influence defect clustering, vacancy mobility, and ultimately the kinetics of self-diffusion and precipitation processes in Cr-based alloys.

The influence of RE doping on Cr self-diffusion was subsequently evaluated by computing the migration energy barrier for a Cr atom moving into a neighboring vacancy. As shown in Figure 6, the calculated migration barrier in undoped Cr is 0.974 eV. Upon doping with Ce and La, the barrier increases to 1.374 eV and 1.391 eV, respectively. Although the final state of the migration process may remain thermodynamically favorable, the elevated activation energies indicate that the strong RE–vacancy binding restricts vacancy mobility. This suppression of vacancy transport in turn hinders Cr self-diffusion via the vacancy-mediated mechanism.

In addition, nitrogen diffusion in bulk Cr was investigated by evaluating the migration of nitrogen atoms between neighboring octahedral interstitial sites. The calculated energy barrier for nitrogen migration in pristine Cr is approximately 1.00 eV. As shown in Figure 7, this barrier increases to 1.89 eV for Ce-doped and to 2.19 eV for La-doped systems, respectively. The increased migration barriers suggest that RE atoms can locally impede nitrogen mobility, likely due to short-range interactions or lattice distortion in their vicinity. The higher energy barrier near La is due to its larger atomic radius, which induces stronger local lattice distortion, narrowing the interstitial path at the migration saddle point and thus hindering nitrogen diffusion. Similar nitrogen-trapping effects have been reported in other RE-doped systems, where RE solutes tend to form so-called “Cottrell atmospheres”, thereby reducing the long-range diffusion of light interstitial elements such as nitrogen or carbon [29,30].

In summary, while RE doping facilitates nitrogen adsorption and near-surface incorporation, its impact in the bulk is twofold. First, strong RE-vacancy binding localizes vacancies near RE atoms, reduces the population of free vacancies, and raises nearby migration barriers, thereby slowing vacancy-mediated Cr self-diffusion. At the same time, a bound vacancy can drag the RE solute via exchange, so the effective RE mobility may increase relative to that of the isolated solute. Second, for interstitial nitrogen, an isolated RE (especially the larger La) introduces stronger local lattice distortion, raising the N migration barrier. However, near the RE-vacancy pair the dilatational strain of the RE and the contractive strain of the vacancy partially cancel at the N saddle, so the RE-induced hindrance is mitigated compared with the isolated-RE case. These results provide a mecha-

nistic understanding of how RE elements simultaneously stabilize nitrogen-rich regions while limiting deep nitrogen penetration, providing insights into how to manipulate the nitridation microstructure by controlling rare earth doping. These conclusions apply to the early stages of nitriding on clean Cr surfaces. After a continuous nitride layer forms, the kinetics are expected to be controlled by defects and electronic structure within the nitride, nitrogen transport through the nitride, and nitride/metal interfacial processes.

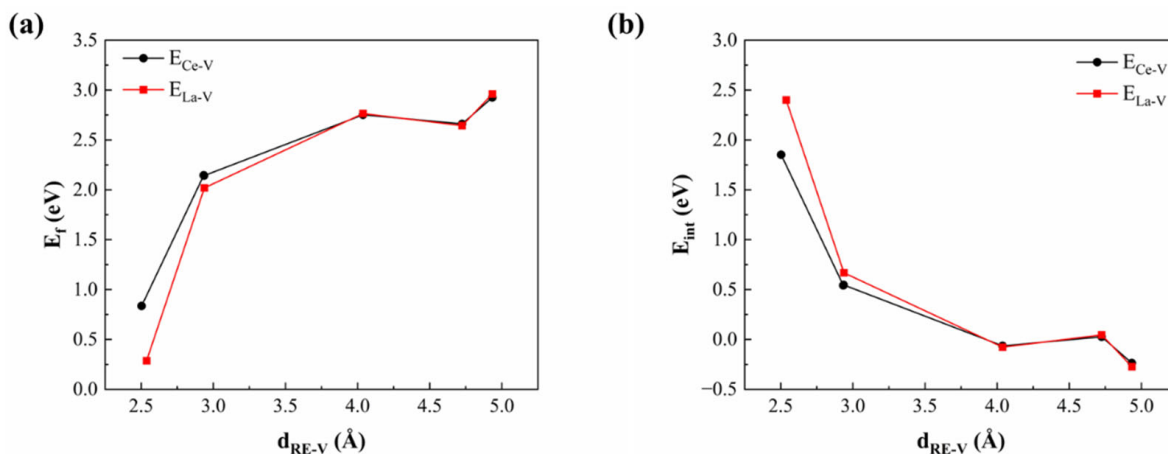


Figure 5. (a) Vacancy formation energy (E_f) as a function of RE-vacancy spacing in bulk Cr lattice. (b) shows the binding energy of the RE-V pair as a function of the RE-vacancy distance.

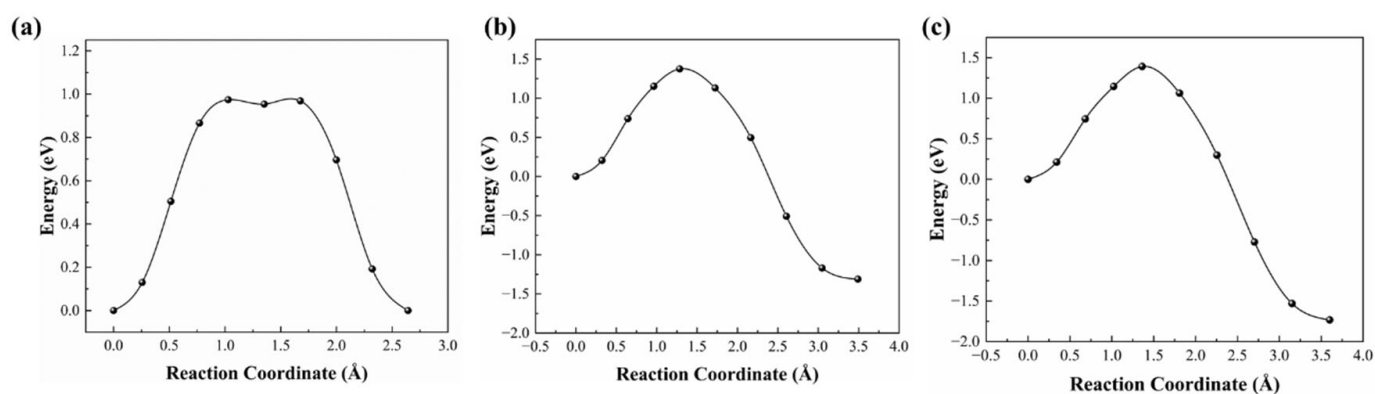


Figure 6. Migration energy barriers for Cr self-diffusion via the vacancy mechanism in (a) pristine Cr, (b) Ce-doped Cr, and (c) La-doped Cr. The initial and final configurations correspond to a Cr atom hopping into a nearest-neighbor vacancy.

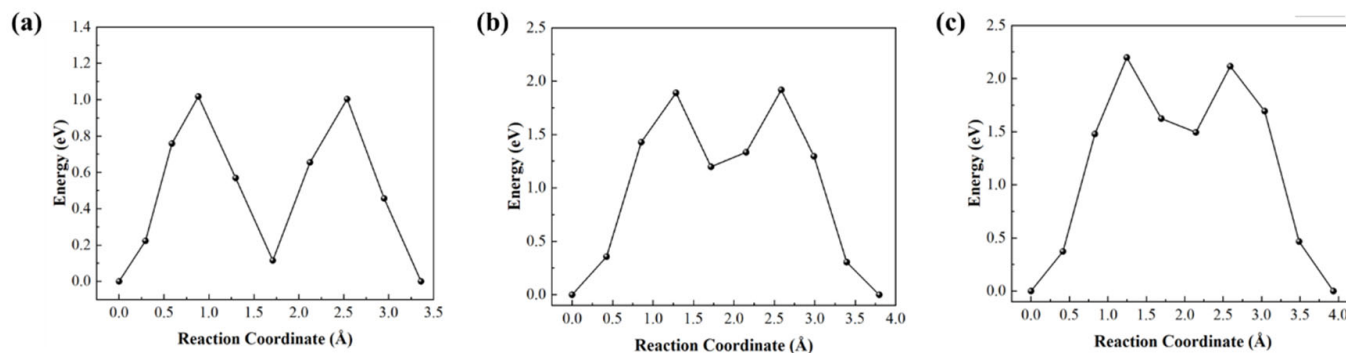


Figure 7. Energy barriers for interstitial N diffusion between adjacent octahedral sites in (a) pristine Cr (b) Ce-doped Cr, and (c) La-doped Cr.

4. Conclusions

In this study, the catalytic effects of Ce and La doping on nitrogen transport behavior in Cr systems were investigated through first-principles calculations. By explicitly elucidating how rare-earth elements precisely regulate nitrogen adsorption, incorporation and diffusion during the early nitriding within Cr, it is revealed that:

Rare-earth (RE) doping at surface sites enhances nitrogen adsorption and slightly lowers the energy barrier for nitrogen penetration into the Cr subsurface, promoting initial nitrogen incorporation.

RE doping in the bulk Cr lattice significantly reduces vacancy formation energies but increases migration barriers for both Cr and nitrogen atoms, indicating strong RE–defect interactions that hinder long-range diffusion.

The overall effect of RE doping is dual: it facilitates nitrogen uptake at the surface while impeding nitrogen and vacancy mobility in the bulk, which may contribute to enhanced surface stability and controlled diffusion depth during nitriding. This well-regulated nitridation process directly supports the development of Cr-based coatings with improved corrosion resistance, addressing the core issue of premature corrosion failure highlighted in the study background.

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