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Dopant-driven electronic and lattice softening enables transport-coupled CO₂ reduction in β -Ag₂Se

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Lanthanide-driven lattice softening provides an integrated framework to couple electronic transport, phonon dynamics, and surface reaction kinetics in β -Ag₂Se. First-principles calculations reveal that La and Gd incorporation induces a near-metallic electronic structure, where dopant d/f states hybridize with Se p orbitals to generate a continuous density of states at the Fermi level, enhancing carrier delocalization and electrical transport. This electronic reorganization weakens lattice restoring forces, reducing the bulk modulus from ~ 77 GPa in pristine Ag₂Se to ~ 23 GPa in LaAg₂Se before partially recovering to ~ 52 GPa in GdAg₂Se. The softened lattice exhibits low-frequency acoustic phonon behavior and increased polarizability, indicative of stronger electron–phonon coupling and modified thermoelectric transport characteristics. Such vibrational flexibility simultaneously facilitates CO₂ activation. Climbing-image nudged elastic band calculations show a significant reduction in the *COOH formation barrier in doped systems, arising from cooperative lattice relaxation and metallic electron donation that stabilize the transition state. Despite elastic softening, positive stiffness eigenvalues and controlled elastic anisotropy confirm mechanical stability. The coexistence of metallic conductivity, lattice polarizability, and soft phonon modes enables dynamic adsorbate accommodation while preserving transport functionality. These findings establish lanthanide-modified β -Ag₂Se as a transport-coupled platform in which lattice softness, carrier density, and phonon engineering jointly govern thermoelectric behavior and catalytic reactivity.

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1 Introduction

Low-temperature, near-zero-bandgap β -Ag₂Se is gaining attention as a catalytic and electrocatalytic platform due to its strong spin–orbit-coupled electronic structure.¹ Elevated electrical conductivity, anisotropic carrier mobility, and topological surface or surface-like states facilitate effective charge separation and directional carrier transport to adsorbate, therefore reducing surface recombination and improving turnover. Microstructurally textured β -Ag₂Se thin films and nanorod arrays, initially optimized for thermoelectric applications, exhibit that regulated grain orientation and columnar structures can integrate high carrier mobility with mechanical durability and cycling stability under bending, highlighting their

appropriateness for scalable catalytic electrodes and membranes.^{2–4} In photo(electro)catalytic systems, β -Ag₂Se can serve as either an active component or a chemically compatible conductive substrate that enhances metal–support interactions, stabilizes single-atom or sub-nanometer cocatalysts, and promotes directional charge transfer across semiconductor/cocatalyst/liquid interfaces, similar to Ag-based and molecular CO₂ reduction platforms where engineered interfaces influence intermediate binding and selectivity.^{5,6} Informed by chalcogenide electrocatalysis, adjusting the near-Fermi-level electronic structure and creating heterointerfaces is anticipated to improve the adsorption energies of critical intermediates (*H, *CO, *COOH, *OOH) and reduce kinetic barriers, akin to interface/d-band engineering techniques employed to augment hydrogen evolution reaction (HER) on Ru–chalcogenide and Ru/metallene systems through regulated heterointerfaces and dopant-induced modulation of water and hydrogen binding.^{7–10} The proven processability of β -Ag₂Se into dense films, nanowires, and nanorod arrays, along with its integration into flexible composites, facilitates the combination of its electronic anisotropy with engineered wettability surfaces and gas–liquid–solid contact configurations to enhance reactant

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accessibility, product desorption, and mass transport. Ultimately, the defect-tolerant chalcogenide lattice and dopant-adjustable density of states near the Fermi level position β -Ag₂Se as a flexible host for atomically precise single-atom and cluster motifs, providing a means to systematically differentiate size and ensemble effects and to leverage intraparticle synergism in intricate multi-step catalytic processes.¹¹

Lattice softening, characterized by a decrease in elastic constants and the emergence of low-frequency soft phonon modes ($\omega \propto \sqrt{k/m}$ with diminished effective force constant k), can be utilized in CO₂ reduction catalysis due to the enhanced electron–phonon coupling, increased lattice polarizability, and more mobile anion sublattices associated with softer lattices. In strained oxides and metals, including lattice-distorted Ni(OH)₂ nanosheets or perovskite-derived and quantum-dot photocatalysts, tensile or compressive distortion augments CO₂ adsorption, promotes charge separation, and adjusts the binding of critical *COOH/*CO intermediates, consequently reducing overpotentials and enhancing selectivity for CO or formate.^{12,13} Comparable strain-induced lattice expansion at Ag/Ag₂CO₃ or derived-Cu surfaces alters *CO adsorption geometry and disrupts the linear scaling between *COOH and *CO, resulting in wider potential windows and enhanced CO₂RR efficiency.^{14,15} From a phonon perspective, lattice softening diminishes sound velocity and alters phonon dispersion, as evidenced in thermoelectrics where internal strain solely contributes to decreased lattice thermal conductivity;¹⁶ in catalysis, this results in soft modes that stabilize dynamically distorted, bent CO₂^{δ−} configurations and offer supplementary non-adiabatic pathways for proton–electron transfer. Lanthanide doping is an effective method for engineering soft, defect-rich lattices: the substantial ionic radii and variable valence of Ln³⁺ induce tensile strain and local bond softening, facilitate oxygen-vacancy formation, and generate strongly basic, polarisable sites that activate CO₂, as evidenced in Ca–CeO₂ supports for Ni/Ca_xCe_{1−x}O_y methanation and La-modulated Ni–LaO_x hybrids, where vacancy-rich, moderately basic sites are associated with optimal low-temperature CO₂ conversion and high selectivity.^{17,18} In co-lanthanide oxides, systematic alterations in lanthanide radius and basicity modulate the product distribution between CO (RWGS) and methane, demonstrating a synergistic interaction between lanthanides and cobalt, as well as a robust structure–activity relationship.¹⁹ At the electronic level, the hybridization of lanthanide 4f–5d6s with chalcogen or oxide ligands influences defect states and adsorbate binding energies, establishing a universal orbital-chemistry mechanism for improved catalysis. Applying this concept to CO₂ electro-reduction, atomic Gd dopants in CuO_x generate tensile strain that stabilizes Cu⁺, enhances CO₂ activation, and reduces the barrier for C–C coupling, resulting in exceptionally high C₂⁺ faradaic efficiencies, while alloy-type tensile strain in Cu–Ag or analogous systems adjusts the d-band center and *CO binding to promote multi-carbon products.^{20,21} Lattice softening and soft-phonon engineering, typically accomplished *via* strategic lanthanide doping, provide a coherent design approach to integrate strain, vacancies, and electron–phonon interactions.

This integration aims to stabilize activated CO₂ intermediates, disrupt detrimental scaling relations, and enhance both activity and selectivity in CO₂ reduction catalysis.

Incorporating lanthanides into Ag₂Se in a systematic way improves its electrical, structural, and thermoelectric properties. This approach enhances catalytic efficiency by allowing aliovalent charge management, adjusting site-specific adsorption, and making it easier to design defects and strain.^{22,23} Adding Gd³⁺ or La³⁺ can change the Fermi level and the states at the band edges, which can change the binding energies of adsorbates. This method is like how rare-earth elements are used to change the lattice fields, local symmetry, and charge density at active sites in different inorganic materials to improve their electrical and catalytic capabilities.^{24,25} Gd³⁺, possessing localized 4f moments, can facilitate the introduction of spin-polarized states and magnetic exchange, which influence spin-sensitive electron transfer processes and the stabilization of intermediates in multi-electron reactions (such as OER/CO₂RR).²⁶ Additionally, it can induce mass and strain fluctuations that lead to the formation of extra catalytic defect sites and may help in reducing parasitic recombination. La³⁺, functioning as a nonmagnetic donor, enhances conductivity and provides oxophilic coordination environments that can modulate *OH/*OOH binding in a precise manner, facilitating the steering of reaction pathways and selectivity.^{27,28} At the interface level, lanthanide dopants can function similarly to heteroatom promoters in chalcogenide systems, shifting the effective d-/p-band centres of active ensembles at Ag₂Se-metal or Ag₂Se-cocatalyst junctions to optimize the Sabatier balance for *H and H₂O. In addition to intrinsic effects, the incorporation of lanthanides works in conjunction with the control of microstructure, such as texture, columnar grains, and the creation of mechanically robust films, to stabilize atomically dispersed metals or bimetallic nanoclusters on Ag₂Se.² This approach allows for the formation of precise, site-isolated motifs, where the intraparticle synergism plays a crucial role in determining activity and selectivity. Overall, Gd/La doping provides a flexible range of parameters, such as carrier density, spin/oxophilicity, strain/defects, and interfacial energetics. These can be co-optimized with heterointerface and wettability design, using data-driven screening and mechanism-aware ML algorithms, to speed up the search for high-performance Ag₂Se-based catalysts for sustainable energy conversion and environmental cleanup.

2 Computational details

The plane-wave pseudopotential version of Quantum ESPRESSO was used for all electronic structure computations within the framework of density functional theory (DFT).²⁹ The generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE) formulation, which offers trustworthy structural and electronic descriptions for chalcogenide systems with mixed ionic–covalent bonding, was used to characterize exchange–correlation interactions. Projector augmented wave (PAW) pseudopotentials were

used to treat core–valence interactions.³⁰ For Ag, La, and Gd, semicore states were specifically added in order to properly represent hybridization close to the Fermi level. Due to the substantial relativistic effects and dopant-induced spin polarization in β -Ag₂Se, a spin-polarization was applied in all calculations. The cutoffs for charge density and plane-wave kinetic energy systematically converged at 320–560 Ry and 40–70 Ry, respectively. Stable force evaluation and total energy convergence within 1 meV per atom were guaranteed by final values of 60 Ry for the wavefunction cutoff and 480 Ry for the charge density cutoff. Marzari–Vanderbilt cold smearing with a width of 0.01 Ry was used to treat metallic smearing, stabilising convergence without causing distortions to near-Fermi electronic states. The Monkhorst–Pack k -point meshes used for Brillouin zone sampling were selected based on the size of the supercell. While dense electronic studies used $16 \times 15 \times 15$ meshes to resolve tiny characteristics in the density of states and transport interpolation, bulk computations used a $9 \times 8 \times 8$ grid for self-consistent field (SCF) optimization. Total energies changed by less than 0.5 meV per atom as the k -point density increased, according to convergence tests. A quasi-Newton method based on BFGS was used to carry out structural optimization. Lattice vectors and atomic locations were loosened until total energy differences were less than 1×10^{-8} eV and residual forces dropped below 1×10^{-3} eV Å⁻¹. Before electronic analysis, all doped combinations were completely relaxed. Tetrahedron integration on dense k -grids was used to do non-self-consistent calculations that yielded electronic band structures and projected density of states. Identification of dopant 4f/5d contributions and their hybridization with Ag-d and Se-p orbitals was made possible by spin-resolved projections. Using a grid spacing that matched the SCF cutoff, charge density difference calculations and electron localization function (ELF) mapping was used to analyze charge redistribution. The climbing-image nudged elastic band (CI-NEB) approach was used to study reaction energetics for CO₂ reduction. Prior to building the reaction pathway, the initial and final adsorption geometries were separately optimized. Convergence was attained when perpendicular forces decreased to 0.02 eV Å⁻¹. Each pathway used seven intermediate pictures, coupled by spring forces of 0.3 eV Å⁻².

Finite-displacement phonon computations interfaced with Phonopy were used to assess lattice dynamical stability. Using strongly converged SCF computations with a $4 \times 4 \times 4$ k -mesh and an energy convergence threshold of 1×10^{-8} Ry, force constants were calculated from $2 \times 2 \times 2$ supercells.³¹ Soft vibrational modes and dopant-induced lattice flexibility were identified by calculating phonon dispersions along high-symmetry routes. Over the range of 0–1000 K, temperature-dependent Helmholtz free energy, entropy, and constant-volume heat capacity were calculated using the harmonic approximation. BoltzTraP2's semiclassical Boltzmann transport formalism was used to assess electronic transport features.³² The temperature-dependent Seebeck coefficient, electrical conductivity per relaxation time (σ/τ), and electronic heat transport between 100 and 1000 K in 50 K increments were computed using dense DFT non-SCF interpolated from

$16 \times 16 \times 16$ k -meshes. To assess relative transport trends among doped systems, a constant relaxation time approximation was used. Butler–Volmer kinetics in conjunction with transition state theory was used to simulate the kinetic polarization behaviour arising from barriers.³³ Arrhenius relations were used to calculate reaction rate constants at 298 K with a frequency prefactor of 10^{13} s⁻¹.^{34,35} To highlight relative kinetic patterns rather than absolute magnitudes, current densities were normalized. To evaluate the formation energy (E_f), the Ag₂Se system was taken as a pristine crystal, and its calculated total energy of the system is denoted as E_{pristine} . Moreover, the total energy of the Ln (La and Gd)-doped system has been denoted as E_{doped} , and the chemical potentials of Ag and Ln (La and Gd) were expressed as μ_{Ag} and μ_{Ln} , respectively.³⁶

$$E_f = E_{\text{doped}} - E_{\text{pristine}} + \mu_{\text{Ag}} - \mu_{\text{Ln}} \quad (\text{substitutional doping});$$

$$E_f = E_{\text{doped}} - E_{\text{pristine}} - \mu_{\text{Ln}} \quad (\text{interstitial doping});$$

The elastic stiffness tensor (C_{ij}) was derived utilising the integrated finite strain stress–strain methodology, wherein symmetry-adapted lattice distortions were created automatically.³⁷ A default small strain amplitude of $\pm 0.5\%$ ($\varepsilon = \pm 0.005$) was employed, ensuring the system remained within the linear elastic region and reducing numerical artefacts. The resultant stress responses were analysed to derive the comprehensive elastic tensor. Post-processing and mechanical analysis of the computed C_{ij} tensor were conducted to assess mechanical stability and ascertain macroscopic elastic parameters, including bulk modulus, shear modulus, Young's modulus, Poisson's ratio, and elastic anisotropy. This methodology facilitated accurate characterization of the mechanical response and anisotropic elastic behaviour of the examined system.³⁸

3 Results and discussion

3.1 Electronic structure of pristine and La/Gd-doped Ag₂Se

Low-temperature β -Ag₂Se (Naumannite) exhibits an orthorhombic $P2_12_12_1$ crystal structure, featuring two symmetry-independent Ag atoms and two symmetry-independent Se atoms located at general 4a Wyckoff locations. The determined lattice parameters ($a = 4.45$ Å, $b = 7.08$ Å, $c = 7.76$ Å) closely align with experimental data, suggesting that the optimized model accurately reflects the equilibrium geometry of the host lattice (Fig. 1a).³⁹ The material is composed of Ag–Se zig-zag chains positioned along the b -axis, resulting in an anisotropic structure with flexible local coordination. Partial disorder at the Ag sites induces minor differences in bonding geometry, endowing the lattice with an intrinsic tolerance to local distortions while maintaining overall symmetry. This flexibility is crucial in ascertaining how the structure accommodates dopant species. Pristine Ag₂Se has narrow Ag–Se distances between 2.654 and 2.816 Å, with an average bond length of 2.742 Å, indicating a robust lattice structure.⁴⁰ Following La doping, the Ag–Se bonds extend to 2.71–2.98 Å, with an average increase to

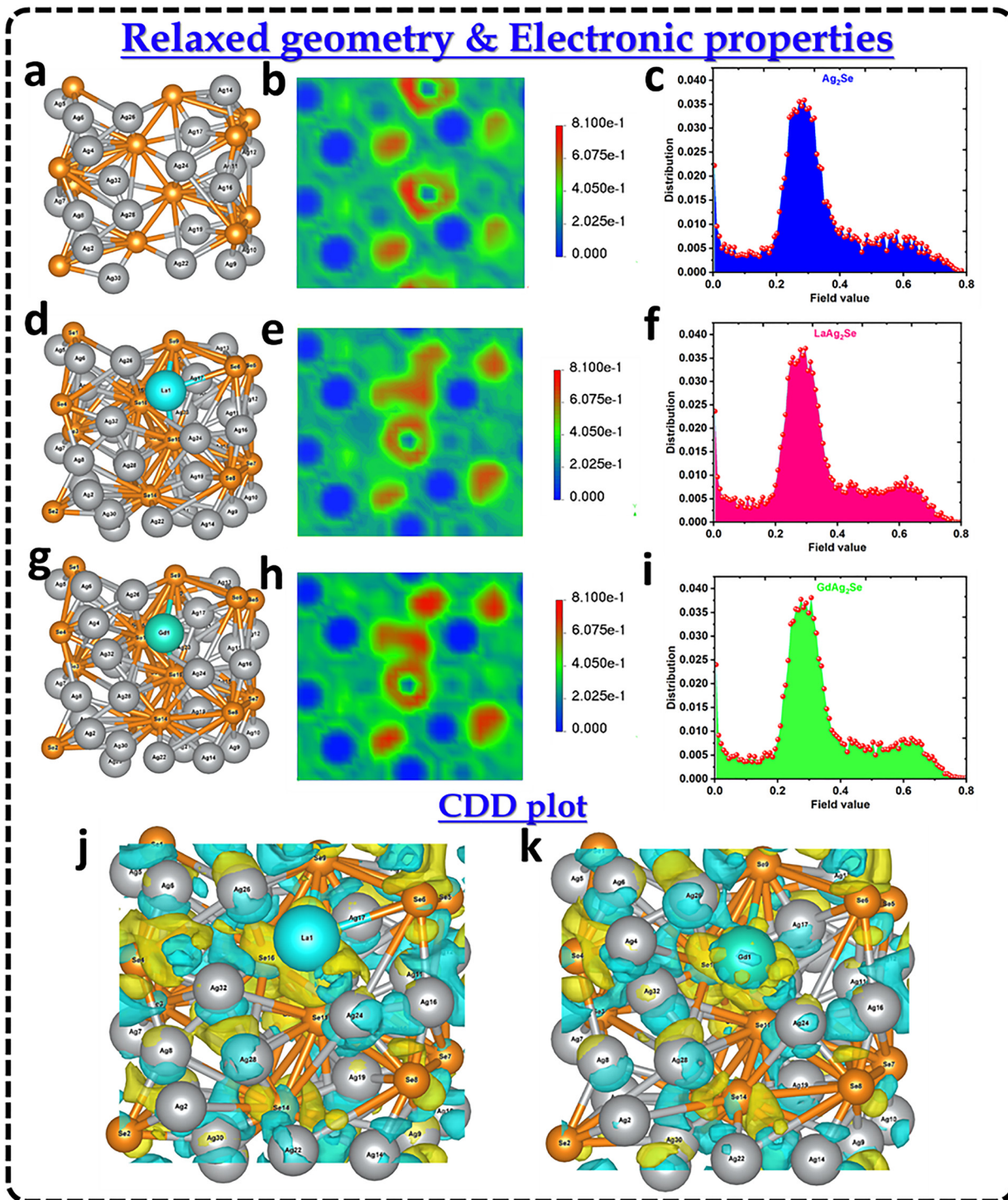


Fig. 1 Relaxed geometries and electronic characteristics of pristine and lanthanide-doped β - Ag_2Se . (a) Optimized structure of pristine Ag_2Se . (b) Electron localization function (ELF) map of the pristine lattice. (c) Corresponding ELF distribution. (d) Optimized structure of La-doped Ag_2Se . (e) ELF map of La-doped Ag_2Se . (f) ELF distribution after La incorporation. (g) Optimized structure of Gd-doped Ag_2Se . (h) ELF map of Gd-doped Ag_2Se . (i) ELF distribution after Gd incorporation. (j) and (k) Charge density difference (CDD) isosurfaces for La- and Gd-doped systems, illustrating dopant-induced charge redistribution. The results highlight enhanced lattice polarizability and dopant-driven electronic redistribution while preserving the structural framework.

2.84 Å, signifying considerable local lattice expansion and augmented structural deformation surrounding the dopant (Fig. 1d).⁴¹ Conversely, Gd doping results in a mild elongation,

with Ag–Se lengths ranging from 2.69 to 2.93 Å and an average of 2.81 Å, indicating regulated lattice disturbance (Fig. 1g).⁴² The emergence of elongated La–Se (~ 3.01 Å) and Gd–Se

(~ 2.87 Å) coordination further substantiates the weakening of bonds and redistribution of strain generated by the dopant. The bond elongations and wider distributions collectively indicate dopant-induced lattice softening, with La causing more expansion and Gd facilitating localized dynamic distortion.²³ Computed formation energy (E_f) values indicate a significant thermodynamic tendency toward interstitial insertion. The insertion of La results in a negative formation energy (-0.92 eV), signifying the spontaneous stabilization of the β -Ag₂Se lattice *via* electronic screening and lattice relaxation, whereas substitutional inclusion is energetically unfavorable ($+1.08$ eV). A comparable hierarchy is noted for Gd, wherein interstitial insertion ($+1.96$ eV) is significantly more stable than substitutional doping ($+3.76$ eV). The approximately 2 eV stability difference indicates a significantly greater equilibrium prospect for interstitial defects, suggesting that dopant incorporation occurs *via* lattice-adaptive insertion rather than host atom substitution.^{43,44} This thermodynamic behavior aligns with the adjustable vibrational response and electronic delocalization inherent to β -Ag₂Se, facilitating the effective integration of interstitial species without compromising the Ag conduction framework. The introduction of La³⁺ or Gd³⁺ dopants result in minimal modification of the orthorhombic framework, indicating that dopant integration is facilitated by localized modifications within the Ag–Se network instead of overall lattice distortion. The local bond angles and distances adjust to accommodate the dopant while preserving long-range periodic order. The crystal framework serves as a stabilizing backbone that facilitates dopant-induced electrical and vibrational alterations while maintaining structural integrity, elucidating the observed defect stabilization and corresponding changes in bonding and functional characteristics. The relaxed structural models indicate that lanthanide doping results in a localized yet cooperative distortion of the Ag–Se framework, rather than a comprehensive lattice collapse. In pristine Ag₂Se, the bonding network appears compact and relatively symmetric, with Ag–Se coordination forming a dense, interconnected scaffold (Fig. 1a). After La incorporation, the local coordination around the dopant expands and visibly perturbs neighboring Ag–Se linkages, introducing bond angle deviations and asymmetric connectivity (Fig. 1d). The doping of Gd generates a comparable local distortion; however, the surrounding network reorganizes more uniformly, indicating structural adaptation rather than disorder (Fig. 1g). This geometric progression indicates that dopant insertion increases local lattice flexibility while preserving the overall framework continuity. The electronic field maps directly reflect this structural perturbation. In pure Ag₂Se, the field intensity exhibits spatial periodicity, characterized by distinct areas of moderate localization that correspond to stable bonding environments (Fig. 1b). The La-doped system shows more irregular field patterns, with enhanced high-intensity regions distributed asymmetrically around the dopant site, indicating stronger local polarization and reduced electronic confinement (Fig. 1e). The Gd-doped lattice, by contrast, demonstrates expanded field localization that remains spatially interconnected, suggesting that

polarization is cooperatively redistributed throughout the lattice rather than restricted to isolated regions (Fig. 1h). This indicates that Gd fosters a stabilized polarizable network instead of solely localized electrical distortion. The histogram distributions corroborate this interpretation. Pristine Ag₂Se displays a relatively sharp peak centered in the mid-field range, consistent with a homogeneous electronic environment (Fig. 1c). La doping broadens the distribution and introduces a more extended tail toward higher field values, signaling increased heterogeneity in local electronic response (Fig. 1f). The Gd-doped profile remains broader than pristine Ag₂Se but is more concentrated than the La case, indicating that polarization enhancement is retained while excessive field dispersion is suppressed (Fig. 1i). This intermediate distribution reflects controlled electronic softness rather than random charge localization. The charge density difference (CDD) maps elucidate the mechanism of redistribution, where the yellow region represents the accumulation of charges and cyan indicates the charge donated region. La doping produces distinct areas of alternating charge accumulation and depletion that extend beyond adjacent bonds, indicating significant dopant-induced polarization (Fig. 1j). In GdAg₂Se, charge redistribution creates smoother, linked channels, indicating cooperative electron reorganization that improves lattice polarizability while maintaining bonding continuity (Fig. 1k).

The determined electronic band structures and associated DOS profiles provide information on how rare-earth doping affects Ag₂Se's electronic characteristics. The narrow gap semi-metallic nature of pure Ag₂Se (Fig. 2a) is reflected in the Fermi level (E_F), which is located just above the valence band maximum.⁴⁵ The modest dispersion of the valence and conduction bands close to the Fermi level suggests that hybridized Ag 4d and Se 4p states dominate the carrier mobility. Its intrinsic metallic characteristic is confirmed by the corresponding DOS, which shows a considerable contribution close to the Fermi level. Subtle band shifting and broadening are seen close to E_F with La incorporation (Fig. 2b). Increased DOS intensity near the Fermi level and a little upward shift in the conduction band edge point to improved electronic delocalization and less bandgap character. This is due to the orbital hybridization between nearby Se 4p and La 5d orbitals, which eases electron excitation and enhances charge transport. On the other hand, a more noticeable change in the near-Fermi band topology is introduced by Gd doping (Fig. 2c). Localized states near the Fermi level are contributed by the partially filled Gd 4f orbitals, which raise the DOS intensity and metallicity. For thermoelectric and catalytic applications where effective charge transfer is crucial, this strong f–p orbital coupling may be advantageous since it increases carrier density and electronic conductivity. Overall, by introducing narrow donor states and changing the local band curvature, both La and Gd dopants influence the Ag₂Se electrical framework. The spin-polarized PDOS plots of pristine Ag₂Se indicate that the valence band region primarily consists of Se-4p and Ag-4d orbitals, with lesser contributions from Ag-5s states (Fig. S1a). The states near the Fermi level are primarily influenced by hybridized

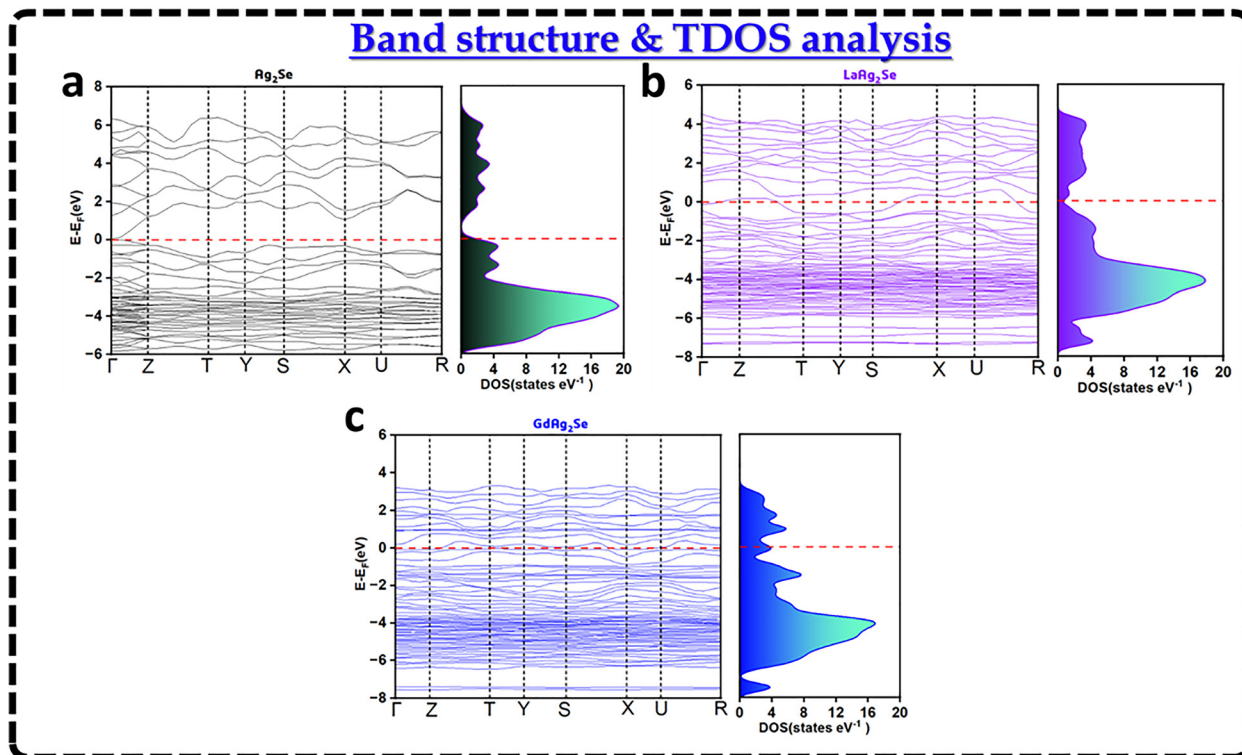


Fig. 2 Electronic band structures and total density of states (TDOS) of pristine and lanthanide-doped β -Ag₂Se. (a) Band structure and TDOS of pristine Ag₂Se. (b) Band structure and TDOS of La-doped Ag₂Se. (c) Band structure and TDOS of Gd-doped Ag₂Se. The red dashed line denotes the Fermi level, highlighting dopant-induced modifications in the electronic states near the band edges and enhanced density of states around the Fermi level.

Ag–Se orbitals, thereby confirming the nature of mixed covalent–metallic bonding. The symmetric profiles of spin-up and spin-down suggest a non-magnetic ground state characterized by semimetallic behavior. In La-doped Ag₂Se (top right), new states emerge near the Fermi level, attributed to La-5d orbitals, along with a minor asymmetry between the spin channels (Fig. S1b). This indicates the emergence of weak spin polarization caused by the La dopant. The proximity of La-5d and Se-4p states to E_F promotes charge delocalization, decreases the electronic bandgap, and aids in electron transport. In Gd-doped Ag₂Se, Gd-4f and 5d orbitals create significant localized states near E_F , leading to enhanced spin asymmetry and increased DOS intensity at the Fermi level (Fig. S1c). This indicates substantial hybridization between Gd-4f/5d and Se-4p states, resulting in magnetic polarization and improved electrical conductivity. The comparative PDOS overlays illustrate the evolution of Ag-d, La-d, and Gd-d states, indicating that the dopant d-states shift closer to E_F and interact with Ag-d orbitals (Fig. S1d). This coupling effectively adjusts the electronic structure, reducing the energy gap between valence and conduction states. The calculated d-band center values provide additional support for this observation: The La and Gd d-states are located at -11.66 eV and -10.83 eV, respectively, which are notably shallower than the Ag-d state at approximately -20 eV (Fig. S1e). The increase in the d-band center indicates improved orbital hybridization and decreased electron localization, which enhances carrier mobility and catalytic activity.

3.2 Phonon dispersion and lattice dynamics

The phonon dispersion relations of pristine Ag₂Se, LaAg₂Se, and GdAg₂Se offer essential understanding of the lattice dynamical response to lanthanide doping and its implications for transport and catalytic behavior. Pristine Ag₂Se displays a distinct phonon spectrum, with acoustic branches gradually approaching zero frequency at the Γ point and lacking extended imaginary modes throughout the Brillouin zone (Fig. 3a).⁴⁶ The optical modes stay distinct and stable, signifying that the force-constant matrix maintains robust restoring forces and harmonic lattice integrity. This behaviour indicates that undoped Ag₂Se exists in a dynamically stable state with a comparatively rigid vibrational environment. This lattice stiffness indicates restricted structural reorganization during adsorbate contact, aligning with the elevated activation barriers noted in the reaction pathway study. The lack of soft phonon modes indicates that catalytic conversions require greater structural and electronic rehybridization energies. La doping results in localized lattice softening, evident as shallow imaginary branches concentrated in the low-frequency acoustic and mixed acoustic-optical regions (Fig. 3b). The soft modes are spatially confined rather than widespread over the Brillouin zone, suggesting that La doping disrupts local force constants without inducing global dynamical instability.^{47,48} This softening can be attributed to ionic size discrepancies and symmetry disruption surrounding the dopant center, resulting in localized strain fields and diminished restoring forces.⁴⁹ This is

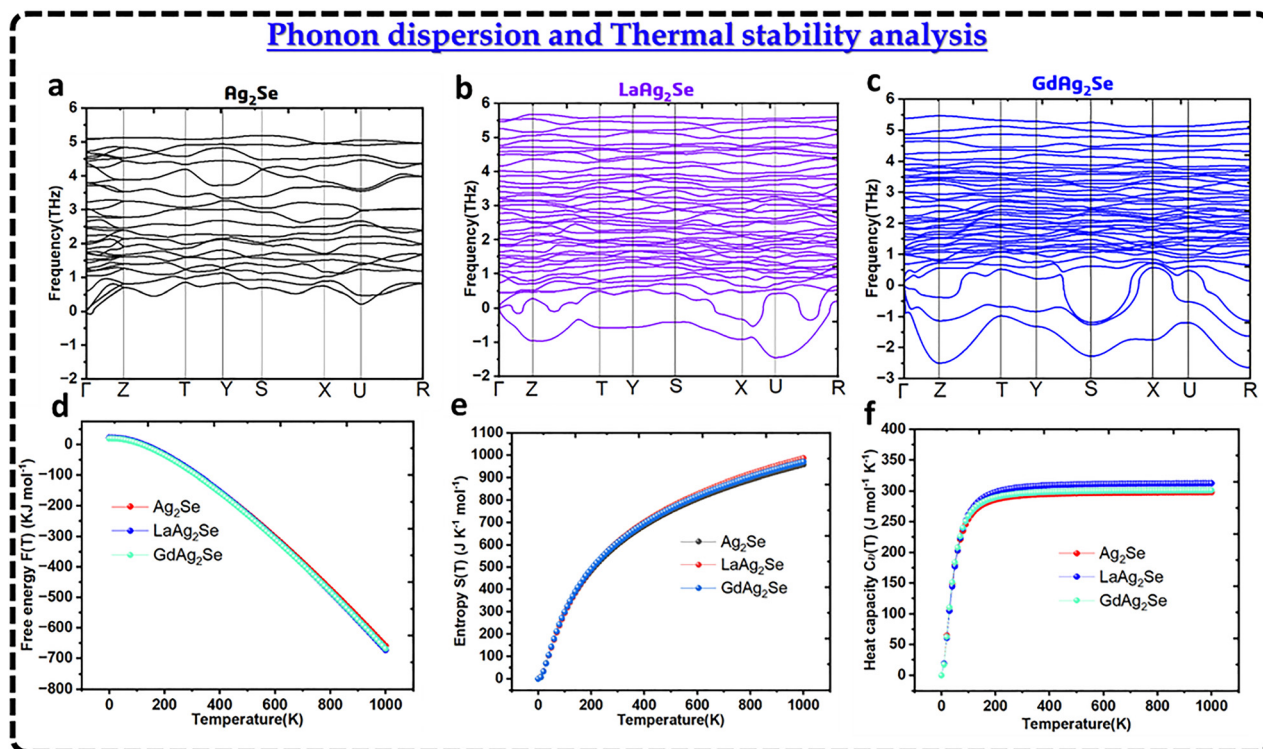


Fig. 3 Phonon dispersion and thermal stability of pristine and lanthanide-doped β -Ag₂Se. (a)–(c) Phonon dispersion relations of pristine Ag₂Se, La-doped Ag₂Se, and Gd-doped Ag₂Se, respectively. (d) Temperature-dependent Helmholtz free energy. (e) Entropy variation with temperature. (f) Heat capacity as a function of temperature. The results highlight dopant-induced lattice softening and enhanced thermodynamic stability across the three systems.

physically evident as increased lattice polarizability and moderate anharmonicity. This behavior facilitates partial structural flexibility during adsorbate binding and intermediate stabilization, aligning with the decreased first activation barrier for *COOH production. The existence of these soft modes indicates heightened phonon scattering and lattice disorder, explaining the diminished bulk transport efficiency and inferior thermoelectric performance compared to the Gd-doped system. Consequently, LaAg₂Se exists in an intermediate dynamical state where localized vibrational flexibility enhances reaction energetics without completely optimizing charge-transport coupling. Gd doping results in a significantly altered lattice response, featuring persistent low-frequency soft modes with greater imaginary amplitudes distributed across various high-symmetry directions (Fig. 3c).⁵⁰ Instead of signifying catastrophic collapse of the structure, these modes demonstrate a superficial vibrational energy landscape linked to dopant-induced strain, mass variation, and robust electronic-lattice coupling resulting from Gd 4f/5d orbital involvement. This soft-mode regime indicates significant lattice flexibility and increased anharmonicity, which can considerably reduce the energy expense of adsorbate-induced distortion. From a catalytic perspective, this vibrational softness facilitates the efficient accommodation of CO₂ bending and hydrogenation processes by diminishing structural reorganization energy and promoting dynamic charge redistribution at the surface. The phonon spectrum thus offers a lattice-dynamical equivalent to the

electronic softening identified in the density-of-states analysis, strengthening the mechanistic connection between dopant-induced polarizability and catalytic efficacy. The observed soft phonon behavior in doped systems should be regarded as metastable lattice flexibility rather than thermodynamic instability. Catalytic reactions emerge at finite-temperature, anharmonic circumstances, where soft vibrational modes can be dynamically stabilized and may enhance reaction kinetics by facilitating structural flexibility and electron-phonon coupling. Within this framework, pristine Ag₂Se serves as a rigid harmonic reference, LaAg₂Se exhibits moderate vibrational polarizability with mixed transport effects, and GdAg₂Se attains a highly flexible lattice that synergistically enhances electronic softness, thermoelectric transport, and transition-state stabilization. The phonon hierarchy reflects the trend in catalytic performance and substantiates the fundamental transport-kinetics coupling model, illustrating that dopant-induced lattice dynamics are crucial for facilitating efficient CO₂ conversion.

3.3 Phonon-based thermodynamic stability

The temperature-dependent vibrational thermodynamic functions obtained from the phonon spectra offer quantitative evidence of how lanthanide doping alters lattice stability and thermal sensitivity in Ag₂Se. The Helmholtz free energy $F(T)$ consistently declines with increasing temperature for all three systems, affirming thermodynamic stability over the examined

0–1000 K range (Fig. 3d). At low temperatures (about 0 K), all structures converge toward zero free energy, signifying similar ground-state vibrational baselines. As the temperature rises, the free energy gradually becomes negative due to contributions from phonon population and vibrational entropy. At 1000 K, pure Ag_2Se attains approximately -670 kJ mol^{-1} , while LaAg_2Se and GdAg_2Se display marginally greater negative values of approximately -685 kJ mol^{-1} and -695 kJ mol^{-1} , respectively.⁵¹ The increasing stabilization in the doped systems indicates improved vibrational contributions due to lattice softening and a heightened phonon density at low frequencies. The smooth curvature and lack of discontinuities demonstrate that dopant-induced soft modes do not cause thermodynamic instability; rather, they enhance a stabilized high-temperature vibrational free energy environment. The entropy $S(T)$ profiles elucidate the influence of dopant-induced lattice flexibility (Fig. 3e). All systems demonstrate the anticipated quick increase in entropy at low temperatures, succeeded by a gradual saturation as higher-energy phonon modes become thermally accessible. At 300 K, the entropy values converge around $600\text{--}620 \text{ J K}^{-1} \text{ mol}^{-1}$, with doped systems slightly surpassing virgin Ag_2Se . At 1000 K, the entropy increases to roughly $980 \text{ J K}^{-1} \text{ mol}^{-1}$ for Ag_2Se , around $995 \text{ J K}^{-1} \text{ mol}^{-1}$ for LaAg_2Se , and approximately $1000 \text{ J K}^{-1} \text{ mol}^{-1}$ for GdAg_2Se .⁵² The increased entropy in doped structures results directly from a heightened population of low-frequency phonons, aligning with the soft vibrational modes noted in the dispersion relations. From a catalytic perspective, enhanced lattice entropy signifies increased configurational and vibrational flexibility, hence promoting structural adaptation during adsorbate attachment and the creation of reaction intermediates. The constant-volume heat capacity $C_v(T)$ exhibits a characteristic Debye-like increase at low temperatures, thereafter, reaching saturation around the classical limit. Below around 100 K, C_v exhibits a substantial rise as acoustic phonons predominate in thermal activation (Fig. 3f).⁵³ At approximately 300 K, all systems attain saturation values near $290\text{--}305 \text{ J mol}^{-1} \text{ K}^{-1}$, with doped structures marginally surpassing virgin Ag_2Se . At elevated temperatures ($\approx 1000 \text{ K}$), the heat capacity at constant volume (C_v) stabilizes at approximately $300 \text{ J mol}^{-1} \text{ K}^{-1}$ for Ag_2Se , around $310 \text{ J mol}^{-1} \text{ K}^{-1}$ for LaAg_2Se , and about $315 \text{ J mol}^{-1} \text{ K}^{-1}$ for GdAg_2Se . The elevated heat capacity in doped systems indicates a greater density of thermally accessible phonon modes, aligning with dopant-induced lattice softening. This improved vibrational heat storage capacity bolsters thermal resilience under catalytic circumstances by mitigating temperature fluctuations and preserving structural integrity. The thermodynamic trends collectively provide a hierarchy of lattice flexibility and vibrational stabilization that corresponds with the phonon dispersion data. Pristine Ag_2Se functions as a somewhat inflexible harmonic lattice characterized by reduced entropy and heat capacity, while the doping of La and Gd progressively enhances vibrational softness and thermal stability. The consistent and gradual temperature dependency of $F(T)$, $S(T)$, and $C_v(T)$ substantiates that the soft phonon modes seen in doped

systems are indicative of metastable anharmonic flexibility rather than thermodynamic breakdown. This vibrational flexibility is mechanistically important for catalysis: softer lattices decrease structural reorganization energy, improve electron–phonon interaction, and facilitate dynamic stabilization of reaction intermediates. The Gd-doped system demonstrates the largest entropy and heat capacity, combined with the most negative high-temperature free energy, thereby offering a thermodynamically stable yet structurally adaptable platform that aligns with its exceptional reaction kinetics and transport–catalysis connection.

3.4 Thermoelectric transport properties

The Seebeck coefficient (S) indicates that pristine Ag_2Se produces the highest thermoelectric driving force, whereas GdAg_2Se exhibits a moderate yet more balanced S due to its enhanced carrier mobility (Fig. 4a).⁴⁶ GdAg_2Se is more suitable for thermoelectric-assisted charge delivery to CO_2RR intermediates. In contrast, LaAg_2Se exhibits a rapidly declining Seebeck response after 250 K. The trends in electrical conductivity demonstrate the benefits of Gd doping, with GdAg_2Se exhibiting the highest conductivity at all temperatures, facilitating rapid electron regeneration during the CO_2 reduction cycle (Fig. 4b). Ag_2Se exhibits moderate conductivity, whereas LaAg_2Se demonstrates increased impurity scattering, which restricts its catalytic applicability. Thermal conductivity is notably elevated in LaAg_2Se , leading to the dissipation of beneficial thermal gradients and a reduction in thermoelectric coupling (Fig. 4c).⁴⁹ GdAg_2Se demonstrates a moderate thermal conductivity that ensures lattice stability while maintaining a sufficient temperature gradient to facilitate thermoelectric-enhanced catalysis. Ag_2Se exhibits the lowest thermal conductivity, yet it does not possess the carrier benefits induced by doping in the Gd system. The power factor indicates that GdAg_2Se is the most efficient thermoelectric material, demonstrating an advantageous relationship between the Seebeck coefficient and electrical conductivity (Fig. 4d). Ag_2Se exhibits a gradual increase but remains inferior, while LaAg_2Se demonstrates consistent lower performance. The figure of merit (ZT) supports this trend, with GdAg_2Se achieving moderate ZT values compared to Ag_2Se at high temperatures, indicating efficient coupling of heat and charge transport (Fig. 4e). LaAg_2Se exhibits a consistently low ZT at high temperatures above 300 K; however, due to the enhanced Seebeck coefficient values at low temperatures, high ZT values were observed until 250 K compared to Ag_2Se and GdAg_2Se . Measurements of the Hall coefficient indicate that GdAg_2Se exhibits the highest carrier concentration, which is crucial for maintaining a continuous supply of electrons necessary for multi-step CO_2 reduction. Ag_2Se exhibits a moderate carrier density, whereas LaAg_2Se demonstrates instability and a decline in RH, which restricts its capacity to support electron-driven reactions (Fig. 4f). Pauli magnetic susceptibility demonstrates the distinct benefit of Gd doping; the pronounced χ response indicates the existence of spin-polarized 4f-derived carriers, which facilitate the stabilization of spin-sensitive CO_2RR

Thermoelectric properties

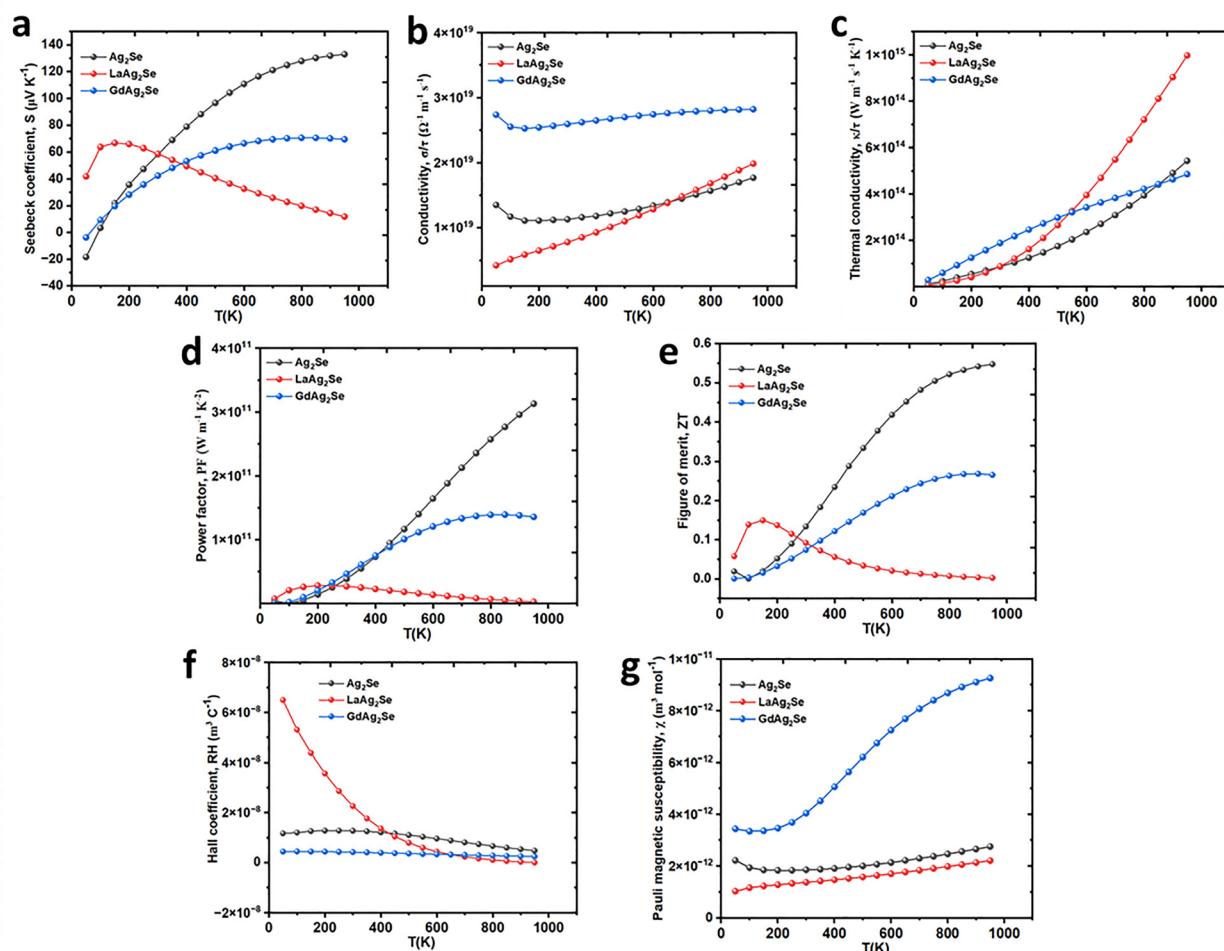


Fig. 4 Temperature-dependent thermoelectric transport properties of pristine and lanthanide-doped β -Ag₂Se. (a) Seebeck coefficient. (b) Electrical conductivity. (c) Electronic thermal conductivity. (d) Power factor. (e) Thermoelectric figure of merit (ZT). (f) Hall coefficient. (g) Pauli magnetic susceptibility. Results highlight dopant-dependent transport modulation, with Gd-doped systems exhibiting improved charge transport and thermoelectric performance.

intermediates (Fig. 4g). Ag₂Se exhibits a moderate response, whereas LaAg₂Se displays a weak and nearly featureless characteristic. The combined thermoelectric, electronic, and magnetic transport behaviors elucidate the superior performance of GdAg₂Se compared to Ag₂Se and LaAg₂Se in thermoelectric-assisted CO₂ conversion, attributed to its optimal balance of carrier density, spin polarization, lattice stability, and charge transport.^{54,55}

3.5 NEB pathway for CO₂ to HCOOH

During the complete conversion of CO₂ to HCOOH, the molecule undergoes a two-stage geometric transformation: the initially linear CO₂ (angle ~ 178 – 180° at the initial state/early intermediate) progressively bends (angle ≈ 125 – 128° at late intermediate/final state) while the C–O and O–H distances reorganize. The C–O bond lengths shift from approximately

1.15–1.20 Å in the initial state to about 1.21–1.36 Å in the later intermediate/final state, while the newly forming C–H/O–H distances shorten to approximately 0.99–1.22 Å at the product stage. The geometric indicators regulate the electronic rehybridization of the C–O unit, thereby influencing the NEB barriers. Pristine Ag₂Se exhibits a near-linear CO₂ geometry for an extended duration along the reaction coordinate, with the C–O angle remaining approximately 178° during the initial intermediate images, collapsing to around 125 – 127° only at a late stage in the pathway. In the transition state region, adsorbate-surface separations are typically greater than 3.5–4.0 Å, while the C–O bond lengths exhibit only minor early elongation (Fig. 5a). The geometric characteristics indicate that CO₂ must experience a significant structural distortion in a single step to attain the reactive bent geometry, characterized by two significant large energy barriers (0.683 and 0.737 eV)

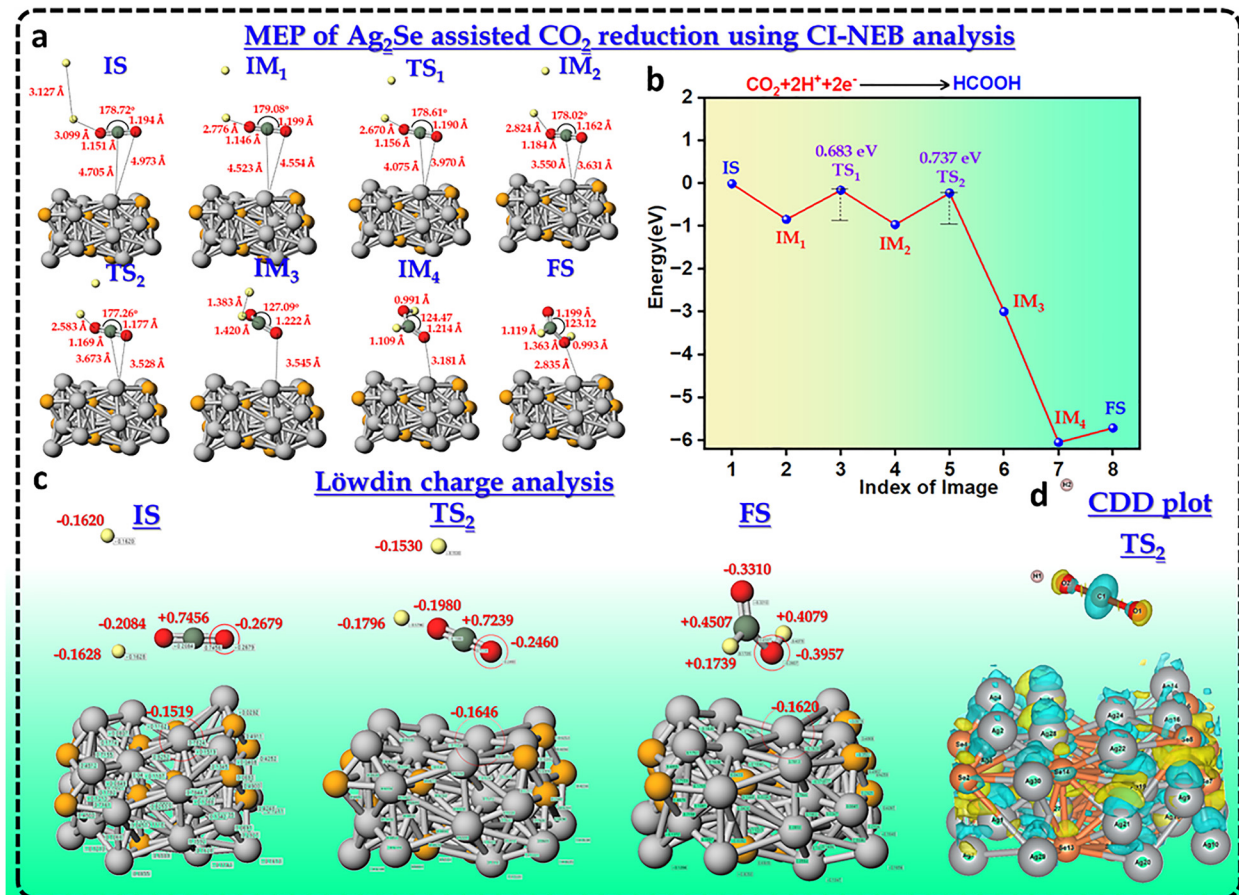


Fig. 5 (a) Minimum energy pathway (MEP) for CO₂ reduction to HCOOH on Ag₂Se obtained from CI-NEB calculations, showing representative atomic configurations from the initial state (IS) through intermediates (IM₁–IM₄), transition states (TS₁, TS₂), and final state (FS), with key bond distances and angles highlighting progressive CO₂ activation and hydrogenation. (b) Corresponding reaction energy profile illustrating the activation barriers and stabilization of intermediates along the pathway. (c) Löwdin charge analysis comparing charge redistribution at IS, TS₂, and FS, evidencing electron transfer and polarization during *COOH formation. (d) Charge density difference (CDD) map at TS₂ visualizing interfacial charge accumulation and depletion associated with adsorbate–surface coupling. The results reveal limited charge transfer and higher activation barriers, indicating less favorable catalytic kinetics on pristine Ag₂Se.

that impede both *COOH formation and the subsequent hydrogenation process (Fig. 5b).^{56,57} The significant geometric distortions surrounding the adsorbed CO₂ suggest that the Ag–Se framework lacks an electronically cooperative environment conducive to charge redistribution. Löwdin charge analysis indicates minimal charge accumulation on the oxygen atoms in TS₂, suggesting that the catalytic centre does not adequately polarize the C–O bond to stabilize the transition state (Fig. 5c). Consequently, Ag₂Se exhibits the lowest kinetic performance, indicating greater activation energy to facilitate the overall reduction. The CDD plot of the TS₂ state revealed the moderate charge redistribution during the stabilization of the transition state (Fig. 5d).

LaAg₂Se exhibits an MEP where the initial bending occurs earlier than in pristine Ag₂Se, though not as early or as closely as in GdAg₂Se (Fig. 6a). At the corresponding transition state, the O···surface distances are shorter than those observed on Ag₂Se (approximately 3.4–3.9 Å compared to larger values on Ag⁵⁸), and the C–O angles decrease to approximately 150–130°

earlier along the reaction pathway. The elongation of C–O bonds and the emergence of C–H/O–H distances suggest partial rehybridization and stabilization of the *COOH intermediate. The Löwdin numbers indicate a moderate electron donation from La, with Δq values smaller than those for Gd but larger than for Ag.⁵⁹ This observation aligns with an oxophilic character that contributes to the stabilization of the early bent geometry. In summary, La alters the local geometry to a degree that reduces the first barrier (0.280 eV), resulting in a more gradual early-stage minimum energy pathway (MEP) compared to Ag₂Se, despite its inferior bulk transport properties (S , σ) (Fig. 6b). Therefore, La aids in chemistry through intermediate stabilization, albeit without offering the same level of continuous electronic replenishment as Gd. LaAg₂Se is situated between Ag₂Se and GdAg₂Se, demonstrating superior performance compared to pristine Ag₂Se, despite having less favorable thermoelectric properties. The NEB profile indicates that the initial transition barrier (0.280 eV) is marginally lower than that of GdAg₂Se, while the subsequent barrier (0.631 eV) is

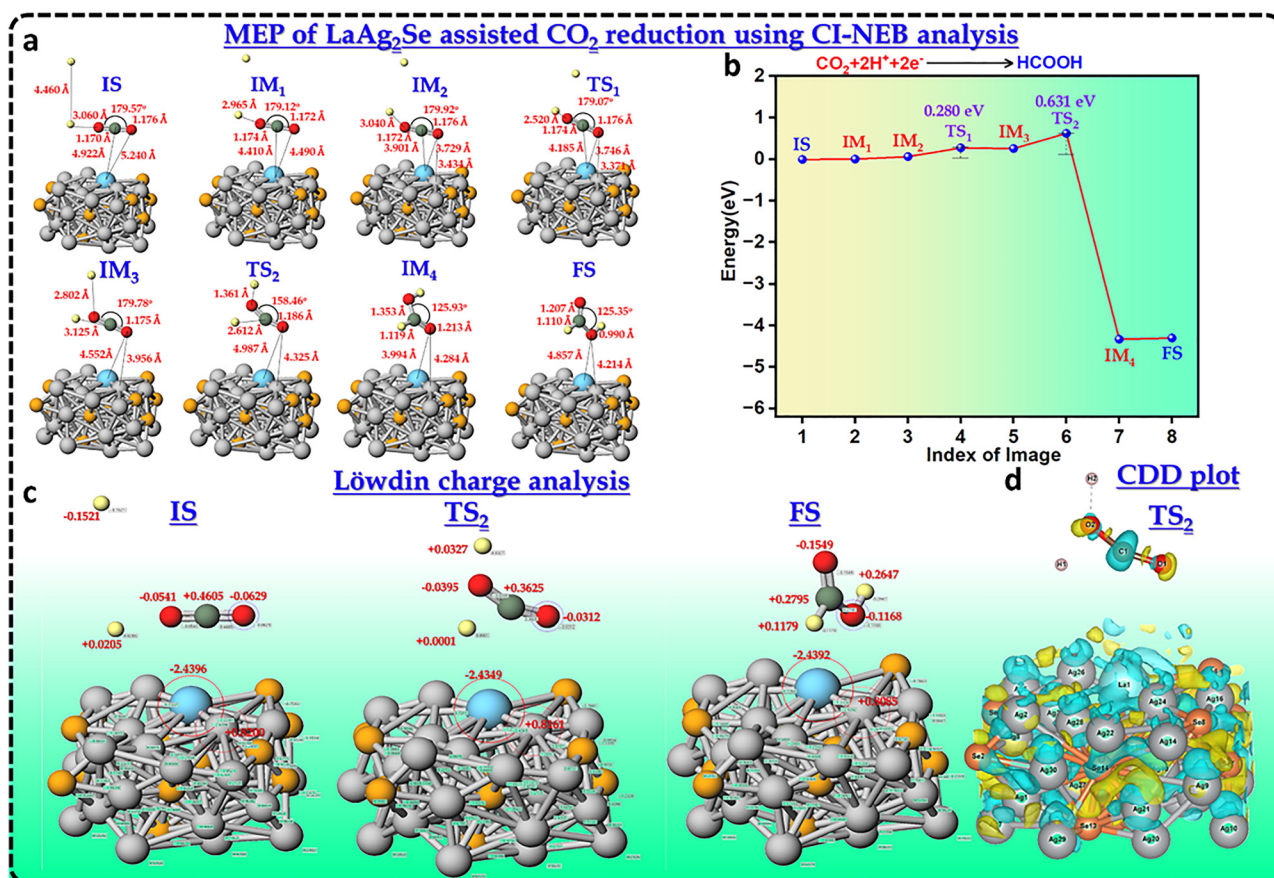


Fig. 6 (a) CI-NEB minimum energy pathway for CO₂ reduction to HCOOH on LaAg₂Se, showing optimized configurations from the initial state (IS) through intermediates (IM₁–IM₄), transition states (TS₁, TS₂), and final state (FS), with selected bond metrics illustrating progressive CO₂ activation and hydrogenation. (b) Reaction energy profile highlighting reduced activation barriers and stabilization of intermediates. (c) Löwdin charge analysis at IS, TS₂, and FS revealing dopant-assisted charge redistribution during *COOH formation. (d) Charge density difference (CDD) map at TS₂ showing interfacial charge accumulation and depletion associated with La-mediated adsorbate–surface interaction. The findings demonstrate moderate barrier reduction and enhanced intermediate stabilization due to dopant-induced electronic polarization.

considerably lower than that of Ag₂Se. This indicates that La doping enhances the electronic environment sufficiently to stabilize the initial *COOH formation step more effectively than the undoped system. Löwdin charge analysis indicates a significant, though weaker than Gd, electron transfer to the critical oxygen atoms in TS₂, which enhances transition-state stabilization (Fig. 6c). Consequently, although La exhibits lower conductivity and thermoelectric performance, its reaction energetics are inherently more advantageous than those of Ag₂Se, as La creates a more polarizable local environment that facilitates CO₂ activation (Fig. 6d). In GdAg₂Se, the minimum energy path indicates that bending and charge redistribution take place earlier and at shorter adsorbate–surface separations compared to other surfaces (Fig. 7a). In the early transition state region, the C–O bond lengths exhibit modest elongation (from approximately 1.17 Å to approximately 1.22 Å), while one oxygen atom approaches the surface to distances near 3.1–3.4 Å. By the later intermediate state, the C–O angle has decreased to below 130°, and the newly forming C–H/O–H distances are significantly shortened to approximately 1.10 Å or less. This initial bending

aligns with a transition state in which (i) the carbon atom exhibits partial rehybridization from sp²-to-sp²/sp³ character, and (ii) the orbitals of the adsorbate oxygen are significantly polarized and hybridized with Gd 4f/5d and surface states. The brief O···surface distances and diminished C–O bond order decrease the energetic expense of reorganizing electron density.⁶⁰ Gd offers geometric anchoring through short contact and favorable bond angles, alongside electronic supply *via* early charge transfer; This combination reduces the energy barrier. GdAg₂Se exhibits a significantly lower energy landscape, characterized by the lowest barriers of 0.291 and 0.465 eV (Fig. 7b). This indicates that the introduction of Gd results in a surface that is inherently favorable for *COOH stabilization and rapid hydrogenation. The presence of Gd 4f/5d orbitals increases electronic softness and polarizability, facilitating continuous charge flow into the O atoms during molecular bending and H-transfer processes. Löwdin charge analysis indicates a significant negative charge accumulation on the *COOH oxygen atoms, confirming effective electron donation from the Gd-coordinated region (Fig. 7c). The cooperative electron

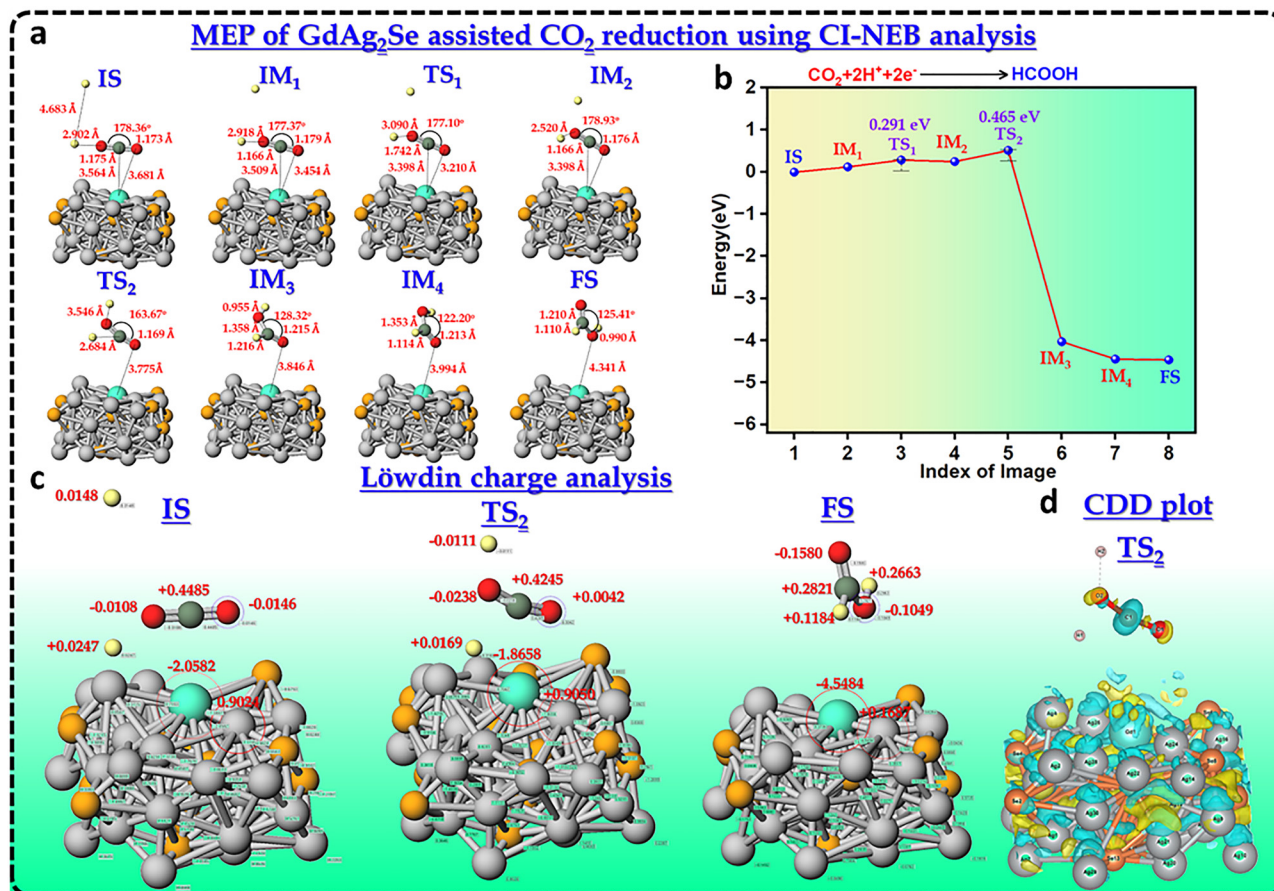


Fig. 7 (a) CI-NEB minimum energy pathway for CO₂ reduction to HCOOH on GdAg₂Se, showing optimized structures from the initial state (IS) through intermediates (IM₁–IM₄), transition states (TS₁, TS₂), and final state (FS), with selected geometric parameters illustrating progressive CO₂ activation and hydrogenation. (b) Corresponding reaction energy profile highlighting dopant-enabled barrier reduction and intermediate stabilization. (c) Löwdin charge analysis at IS, TS₂, and FS demonstrating Gd-assisted charge redistribution during *COOH formation. (d) Charge density difference (CDD) map at TS₂ visualizing interfacial charge accumulation and depletion associated with strong adsorbate–surface coupling. The results indicate the lowest activation barriers and most efficient charge transfer, confirming superior catalytic kinetics in the Gd-doped system.

transfer elucidates why GdAg₂Se exhibits the most favourable kinetics, lowest activation energies, and highest predicted CO₂ conversion activity. The Löwdin charge on Gd increases from -2.0582 to $-1.8658e$ ($\Delta = +0.1924e$) between the initial state and transition state 2, indicating a net loss of electrons at Gd and direct electron donation to the adsorbate region (Fig. 7d). This process stabilizes the transition state and reduces the reaction barrier. Ag₂Se exhibits minimal variation in the density of states throughout the reaction. The states adjacent to the Fermi level are primarily characterized by Ag-d and Se-p states, exhibiting minimal spin polarization. The density of states (DOS) intensity near the Fermi level (E_F) exhibits only a slight increase from IS to TS₂, indicating that the surface offers limited electronic flexibility during CO₂ bending. The absence of significant spin splitting or localized donor states leads to inadequate stabilization of the transition state. In FS, the density of states shifts only slightly, with minimal evidence of hybridization between Ag and the O 2p orbitals. This aligns with your Löwdin charge results, indicating that the oxygen atoms acquire the lowest electron density among the three

systems. Consequently, Ag₂Se functions as a passive surface, resulting in inadequate electron density rearrangement during reaction steps, which contributes to the highest NEB barriers. La introduces 5d states that exhibit delocalization and reduced spin polarization relative to Gd. In the IS, La exhibits a modest density of states near the Fermi level, characterized by reduced splitting between spin channels (Fig. S2a). In TS₂, the La-5d states exhibit a slight shift towards E_F , resulting in an increased DOS slope at E_F and a greater availability of electrons compared to pristine Ag₂Se. La produces a lower early barrier than pristine Ag₂Se, despite having inferior thermoelectric transport properties. In contrast to Gd, La does not significantly distinguish between spin-up and spin-down states at the Fermi level and does not create deep hybridized states during the formation of COOH. The broadened La states in the FS are relatively shallow and exhibit weak coupling to the O-2p orbitals, suggesting moderate yet incomplete charge donation. Consequently, LaAg₂Se facilitates COOH formation more effectively than Ag₂Se, yet less so than GdAg₂Se, aligning with NEB, Löwdin, and catalytic trends. The Gd-containing system exhibits the

most significant near-Fermi reorganization throughout the reaction. At the IS stage, both spin-up and spin-down 4f/5d contributions are situated near E_F and are partially occupied, resulting in a highly polarizable electronic environment. In TS₂, the asymmetry between spin channels is further pronounced, and the density of states (DOS) intensity at the Fermi level (E_F) increases, suggesting that the system efficiently injects electrons into the antibonding orbitals of the bending CO₂ (Fig. S2b). The “softened” electronic structure facilitates *COOH formation; in terms of density of states, this indicates that the surface can consistently supply electrons to the O–C–O unit during deformation. The Gd states in the FS exhibit significant hybridization with O-2p, evidenced by the broadening of peaks between –6 and –2 eV, along with a reduction in Gd spin-up density near –1 eV (Fig. S2c). This represents the electronic fingerprint of effective electron donation, aligning with your Löwdin results (–2.0582 to –1.8658e). The Gd density of states indicates significant spin polarization, facile electron release, and pronounced oxygen hybridization, which elucidates the observed lowest reaction barriers. Analysis of kinetic polarization using barrier-based methods.

3.6 Analysis of kinetic polarization using barrier-based methods

The evaluation of electrochemical activity trends was conducted utilizing a kinetic model based on transition state theory, which was derived from NEB activation barriers. The identification of the *COOH intermediate formation as the rate-determining step was established. Free-energy barriers were estimated as $\Delta G^\ddagger = \Delta E^\ddagger + (\Delta ZPE - T\Delta S)$. Where $\Delta G^\ddagger$ = activation free energy barrier; $\Delta E^\ddagger$ = activation energy barrier; T = temperature (298 K); ΔS = change in entropy; A constant ZPE-entropy correction of 0.25 eV was utilized, as derived from previous CO₂ reduction studies reported in literatures, and was uniformly applied across all systems.^{61,62} The influence of the applied potential was incorporated through a linear electrochemical correction utilizing the computational hydrogen electrode (CHE) framework. The curves produced indicate trends in relative kinetic activity instead of absolute current densities.

Rate-determining step (RDS): * + CO₂ + (H⁺ + e[–]) → *COOH

Free-energy approximation: $\Delta G^\ddagger = \Delta E^\ddagger + 0.25$ eV (constant ZPE – $T\Delta S$ has been adopted in the literature).

Barrier-based kinetic polarization descriptor: $j = j_0[\exp(\alpha F\eta/RT) - \exp(-(1 - \alpha)F\eta/RT)]$; with $j_0 = A \exp(-\Delta G^\ddagger/k_B T)$.⁶³

We applied python-programming script to derive the polarization curves. We employed the aforementioned Butler–Volmer equation and the Arrhenius relation, j_0 . This correlation is the standard approach to model and relate the DFT-derived activation barriers to electrochemical rates. $\eta = U - U_{eq}$ accurately defines the deviation from equilibrium; Since the applied potential (U) is swept from 0 to –1.0 V and $U_{eq} = -0.25$ V, and the overpotential definition correctly covers both the anodic ($\eta > 0$) and cathodic region ($\eta < 0$). $A_{prefactor}$ is the standard frequency factor (10^{13} s^{–1}) resulting in very high raw current densities. Thus, we normalized the current density. This step does not cause a change in the polarization plot, but rather for

absolute comparisons to experimental data, and this would be affected by the active sites and the electrode surface area, hence it should be scaled to them. Where k = rate constant, k_B = Boltzmann constant (8.617×10^{-5} eV K^{–1}), T = absolute temperature (298 K).

Potential dependence (CHE-based, qualitative analysis)

$$\Delta G^\ddagger(U) = \Delta G^\ddagger(0) - \alpha e(U - U_{eq});$$

where $\Delta G^\ddagger(U)$ = potential-dependent activation free energy barrier for the rate-determining step at applied potential (U).

Fig. 8a and b correlate dopant-induced lattice softening to interfacial reaction kinetics in the production of *COOH. Pristine Ag₂Se, characterized by a somewhat rigid bonding framework, has the slowest cathodic current increase in the Butler–Volmer polarization curves, indicating more kinetic resistance and restricted structural flexibility for transition-state stabilization. The addition of lanthanides diminishes the lattice rigidity by reducing the Ag–Se restoring forces, hence facilitating increased atomic relaxation around the reactive species. This results in an earlier onset of current and more pronounced polarization slopes. LaAg₂Se demonstrates a distinct kinetic enhancement, but GdAg₂Se exhibits the most significant response, aligning with its reduced estimated transition-state barriers (~0.291 eV and ~0.465 eV) and increased lattice flexibility that promotes electron injection into the activated CO₂ intermediate. Fig. 8c elucidates this kinetic evolution *via* the volcano-type activity map, which associates catalytic performance with *COOH binding strength. The rather inflexible lattice of Ag₂Se categorizes it into a weaker-binding domain (about –0.75 to –0.80 eV), where inadequate intermediate stabilization results in sluggish polarization behaviour. Dopant-induced lattice softening alters adsorption energetics to achieve an optimum equilibrium. LaAg₂Se (~–0.65 eV) offers partial stabilization, whereas GdAg₂Se nears the volcanic apex (~–0.50 eV), where structural flexibility and charge transport are well aligned. The optimized adsorption-kinetic connection elucidates the pronounced polarization response found for GdAg₂Se.

3.7 Transport-kinetics coupling and thermoelectric contributions

Thermoelectric-based kinetic model: $k(T) \propto \exp(-\Delta G^\ddagger * \text{COOH}/k_B T)$.

$-\Delta G^\ddagger * \text{COOH}$ = activation free energy for *COOH formation.⁶¹

Electrical conductivity from Boltzmann transport: $\sigma(T) = (\sigma/\tau)(T)\tau$. Where σ/τ = conductivity per relaxation time obtained from transport calculations; τ = carrier relaxation time;⁶⁴ transport adequacy ratio: evaluation of the bulk transport sustainability for intrinsic reaction kinetics, we define a transport adequacy ratio as: $\Phi(T) = \sigma(T)/\exp(-\Delta G^\ddagger * \text{COOH}/k_B T)$.⁶⁵ This dimensionless value compares the electron transport capacity to the kinetic demand imposed by the *COOH activation barrier during the CO₂ reduction reaction. In order to eliminate the large orders of magnitude and to compare the existing trend, we applied $\log_{10} \Phi(T)$.

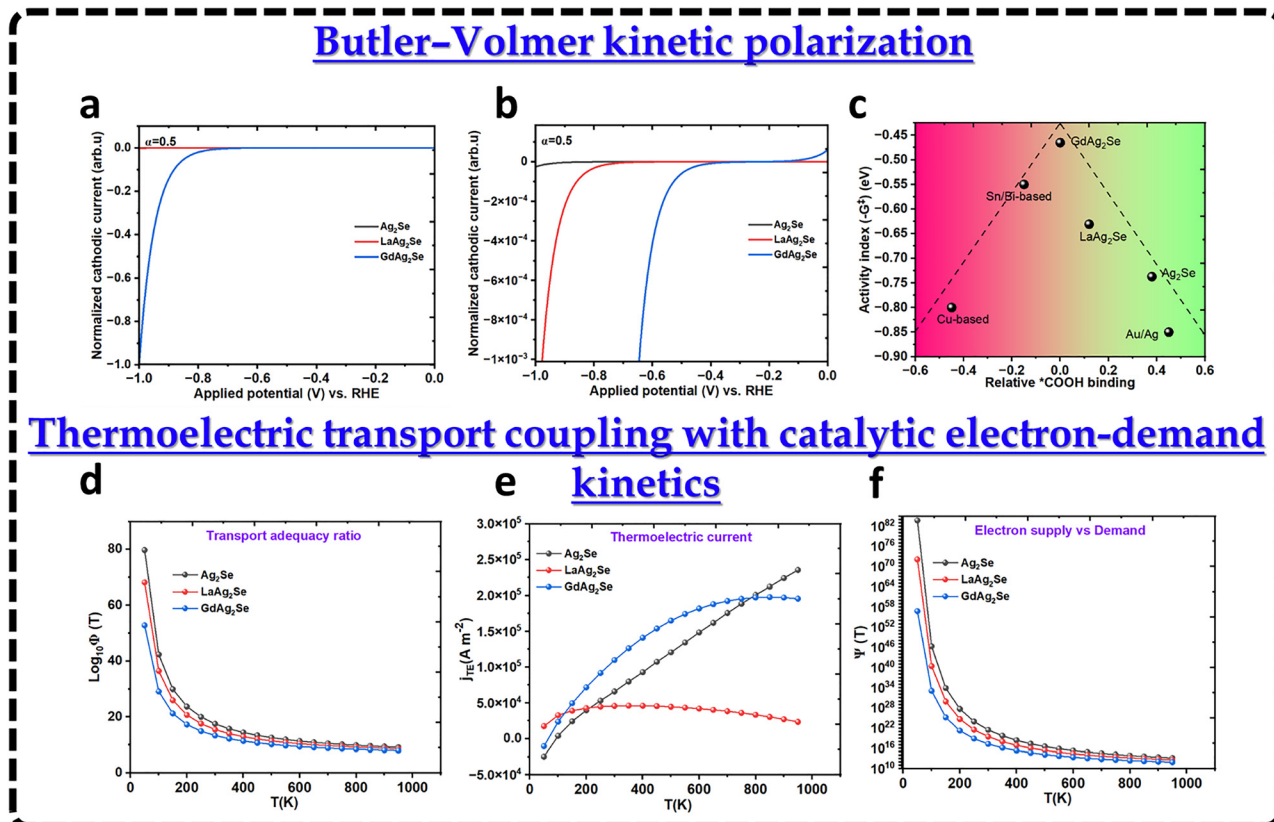


Fig. 8 Butler–Volmer kinetic polarization curves (a) and (b) generated from CI-NEB activation energetics for *COOH production during CO₂ reduction on Ag₂Se, LaAg₂Se, and GdAg₂Se, demonstrating dopant-dependent cathodic current response and charge-transfer efficiency. (c) A volcano-type activity map linking anticipated catalytic activity with relative *COOH binding strength, bringing lanthanide-doped systems nearer to the optimum adsorption range. (d) The transport adequacy ratio illustrates the equilibrium between electron delivery and kinetic consumption, highlighting enhanced coupling in doped systems. (e) Computed thermoelectric current as a function of temperature, illustrating dopant-modulated carrier flux accessible for catalytic turnover. (f) Temperature-dependent analysis of catalytic electron demand in relation to lattice electron supply, emphasizing the extent of transport-reaction alignment. The key findings demonstrate that Gd doping achieves optimal transport–kinetics coupling, leading to superior catalytic performance.

The electron supply rate delivered by the material is approximated as: $j_{\text{supply}}(T) = \sigma(T)E$; E = effective internal electric field; the associated electron supply-to-demand ratio is: $\Psi(T) = \sigma(T)E / \exp(-\Delta G^\ddagger * \text{COOH} / k_B T)$.

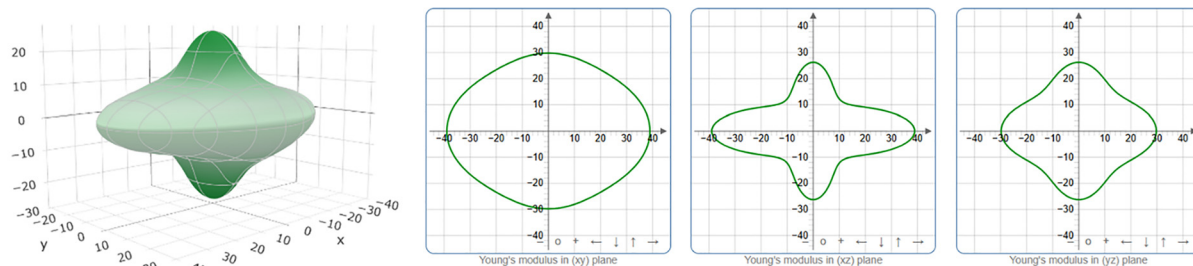
Thermoelectric current density: $j_{TE}(T) = \sigma(T)S(T)\Delta T$. Where $S(T)$ = seebeck coefficient; ΔT = temperature gradient.

Fig. 8d illustrates the temperature-dependent transport adequacy ratio ($\Phi(T)$), which evaluates the bulk charge-transport capacity of the catalysts relative to the intrinsic kinetic requirements imposed by *COOH formation barrier. Throughout the entire temperature spectrum, pristine Ag₂Se demonstrates the highest Φ values, followed by LaAg₂Se and GdAg₂Se. This trend reflects the decreasing activation free energy of *COOH with the incorporation of lanthanides. The significant Φ values observed for Ag₂Se do not imply enhanced catalytic performance; instead, they indicate a reaction-limited regime where charge transport greatly surpasses the inherently slow reaction kinetics. With rising temperature, $\Phi(T)$ exhibits a decrease across all systems, aligning with the increased thermal accessibility of the activation barrier. Fig. 8e illustrates the

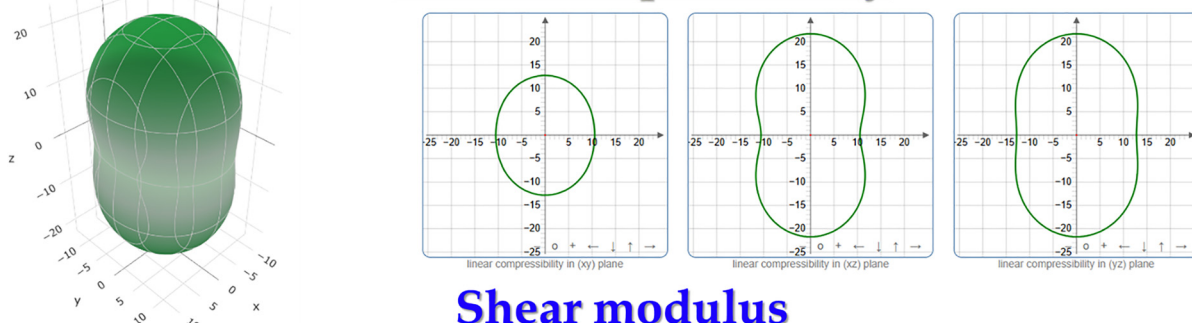
thermoelectric current density, j_{TE} , obtained from the temperature-dependent electrical conductivity and Seebeck coefficient. GdAg₂Se demonstrates a significant increase in j_{TE} with temperature, achieving values that are comparable to or surpass those of pristine Ag₂Se at higher temperatures. This behavior underscores the significance of lanthanide doping in improving thermoelectric transport, thus promoting bulk electron migration in response to a thermal gradient. In contrast, LaAg₂Se exhibits a weaker and non-monotonic thermoelectric response, suggesting a less effective coupling between charge carriers and thermal driving forces. The ratio of electron supply to reaction demand, $\Psi(T)$, illustrated in Fig. 8f, supports this interpretation. At low temperatures, $\Psi(T)$ exhibits significant variation across several orders of magnitude, attributed to the exponential sensitivity of the *COOH activation step to temperature. Ag₂Se demonstrates the highest Ψ values, indicating an oversupply of charge in relation to a significantly kinetically hindered reaction. In contrast, GdAg₂Se exhibits lower yet more balanced Ψ values, suggesting a closer alignment between electron transport and catalytic requirements.

Elastic properties of LaAg₂Se

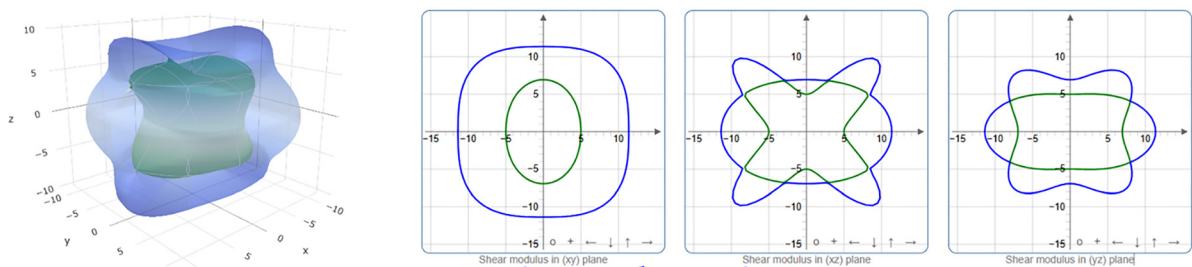
Young's modulus



Linear compressibility



Shear modulus



Poisson's ratio

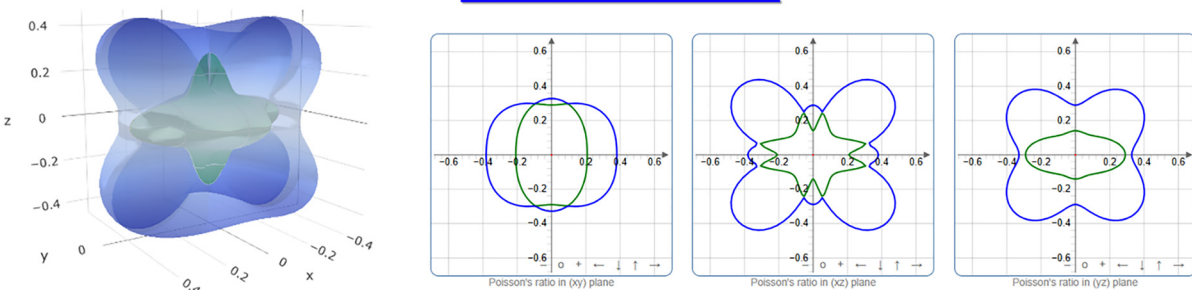
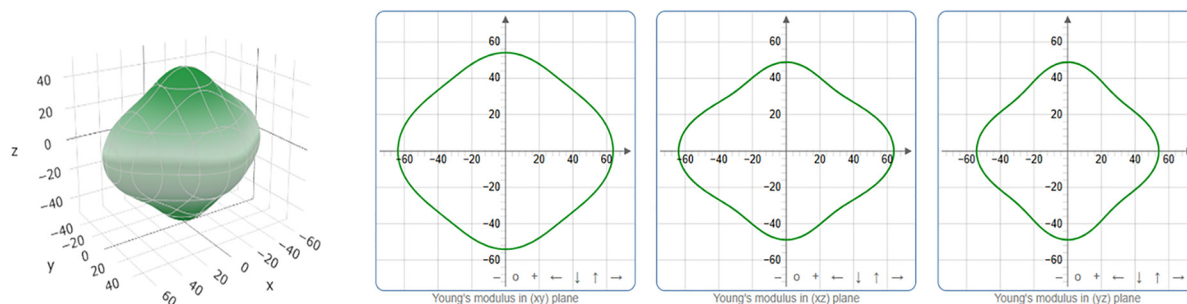


Fig. 9 Directional elastic response of LaAg₂Se showing Young's modulus, linear compressibility, shear modulus, and Poisson's ratio surfaces with planar projections. La substitution produces a mechanically softened lattice with reduced directional stiffness, enhanced compressibility, and lower shear resistance while maintaining elastic stability. The smoother anisotropic distributions indicate increased lattice compliance and strain adaptability, consistent with softened acoustic phonon behaviour and structural flexibility relevant to adsorption-driven surface processes. The results highlight enhanced lattice flexibility that facilitates structural adaptation during catalytic processes.

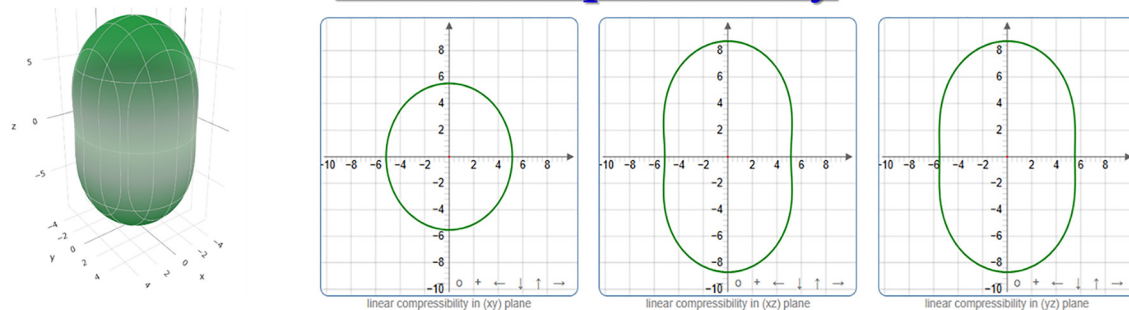
The coupling of transport and kinetics indicates that Gd doping facilitates a more efficient use of the inherently lower *COOH activation barrier, rather than simply enhancing charge availability.^{66,67}

Elastic properties of GdAg_2Se

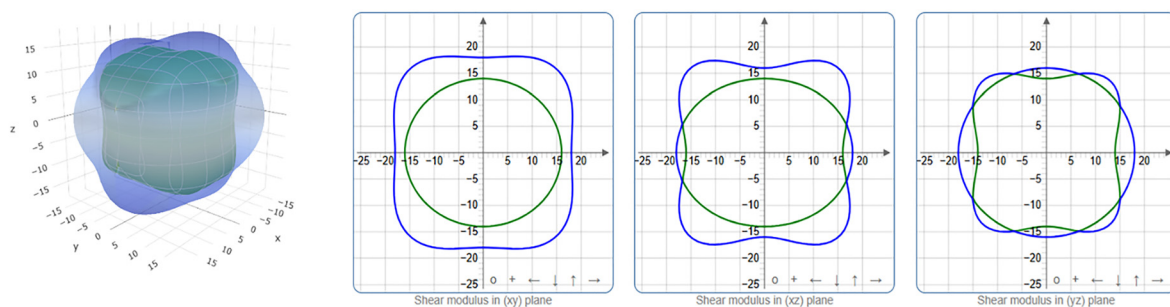
Young's modulus



Linear compressibility



Shear modulus



Poisson's ratio

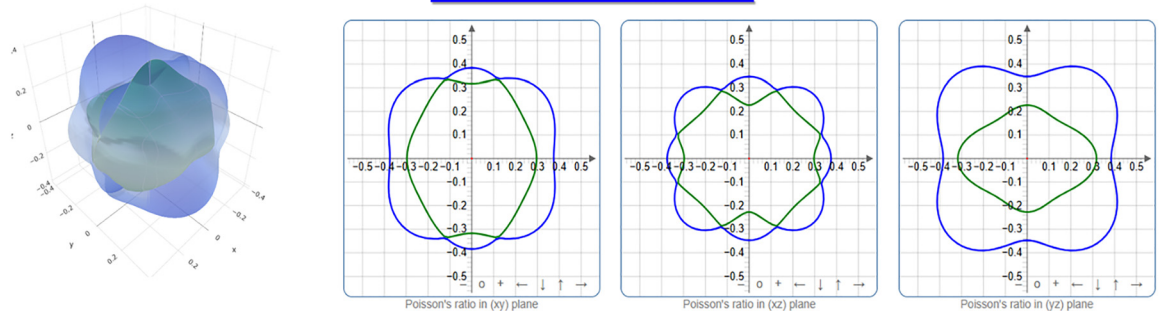


Fig. 10 Directional elastic response of GdAg_2Se exhibiting Young's modulus, linear compressibility, shear modulus, and Poisson's ratio surfaces with planar projections. Gd substitution yields a mechanically stable lattice characterized by intermediate stiffness, moderate anisotropy, and positive compressibility in all directions. The equilibrium shear resistance and regulated elastic coupling suggest a structure that maintains integrity while permitting lattice flexibility, in accordance with stabilized acoustic phonon softening pertinent to adsorption-driven surface phenomena. The results indicate an optimal balance between structural robustness and lattice adaptability for catalytic operation.

3.8 Elastic signatures of dopant-induced lattice softening

The Voigt–Reuss–Hill averages indicate a distinct stiffness development. Pristine Ag_2Se possesses a bulk modulus of approximately 77 GPa, a Young's modulus of around 39 GPa, and a shear modulus of about 14 GPa, signifying a lattice that withstands volumetric compression while exhibiting modest shear compliance (Fig. S3) (Tables S1–S4). The elevated Poisson ratio (~ 0.42) indicates effective elastic strain redistribution, aligning with a bonded structure that can convey mechanical stress without localized deformation. This mechanical profile pertains to rigid acoustic phonon branches, constraining significant lattice distortions. La doping results in significant elastic softening (Fig. 9).⁶⁸ The bulk modulus diminishes to approximately 23 GPa, paralleled by decreases in Young's modulus (around 24 GPa) and shear modulus (approximately 9 GPa). This almost 70% reduction in volumetric stiffness indicates less interatomic restoring forces and increased lattice deformability.

The diminished Poisson ratio (~ 0.32) signifies a decrease in transverse strain coupling, resulting in more localized deformation. This softening directly correlates with low-frequency acoustic phonon modes, resulting in increased vibrational amplitude and anharmonicity. These characteristics facilitate cooperative lattice relaxation, an essential element for adsorption-induced structural modification.⁶⁸ GdAg_2Se resides in an intermediate mechanical domain. The bulk modulus (~ 52 GPa) exceeds that of LaAg_2Se by more than a two-fold, although it remains inferior to that of pure Ag_2Se , signifying a partial restoration of lattice rigidity (Fig. 10). The Young's modulus (~ 48 GPa) and shear modulus (~ 18 GPa) surpass those of both parent phases, indicating improved resistance to directed and shear deformation. The Poisson ratio (~ 0.35) resides within a conventional elastic range, signifying equitable strain transfer.⁶⁹ This stabilized stiffness profile reflects controlled acoustic phonon softening: the lattice maintains adequate flexibility for dynamic adaptability while preventing excessive mechanical compliance. The stiffness eigenvalues elucidate the hierarchy of deformation modes. Ag_2Se exhibits a wide eigenvalue range (~ 10 –243 GPa), indicating significant anisotropic stiffness and distinct deformation resistance. LaAg_2Se has a contracted eigenvalue spectrum (~ 5 –71 GPa), signifying low-energy elastic modes that facilitate easy lattice distortion. GdAg_2Se re-establishes this spectrum (~ 14 –158 GPa), reinstating the stiffness hierarchy while maintaining mild deformation pathways. The lack of negative eigenvalues in all instances verifies mechanical stability and precludes elastic instability. Directional Young's modulus analysis reveals that Ag_2Se exhibits strong anisotropy, with modulus variation spanning approximately 16–55 GPa. This anisotropy indicates directional bonding limitations and inflexible lattice segments. LaAg_2Se diminishes this variance (≈ 16 –39 GPa), signifying a more isotropic and flexible structure. GdAg_2Se further reduces anisotropy (≈ 41 –64 GPa) while increasing absolute stiffness, indicating a mechanically balanced lattice that allows for controlled directional deformation. Linear compressibility surfaces

corroborate this perspective. Ag_2Se exhibits anisotropic compressibility associated with rigid bond orientations. LaAg_2Se exhibits increased compressibility in various orientations, in accordance with lattice breathing modes induced by elastic softening. GdAg_2Se exhibits positive compressibility with modest anisotropy, indicating a stable yet flexible structure. The significant softening in LaAg_2Se indicates increased anharmonic lattice motion, promoting structural relaxation during molecule adsorption. Nonetheless, excessive softening poses a risk of mechanical fragility. GdAg_2Se signifies a stabilized soft-mode phase. The elastic constants facilitate low-energy phonon activity that allows for lattice deformation while preserving structural integrity. This equilibrium is essential for catalytic longevity, as recurrent adsorption–desorption cycles require both adaptability and robustness.⁷⁰ The increased shear modulus in GdAg_2Se signifies resistance to permanent deformation, hence promoting catalytic durability. Simultaneously, controlled compressibility and anisotropy facilitate localized lattice modification, enhancing charge redistribution and bond deformation during CO_2 adsorption. Consequently, elastic tuning through lanthanide doping directly influences phonon-assisted catalytic mechanisms. Despite La doping causing a substantial decrease in bulk modulus (~ 77 GPa in pristine Ag_2Se to around ~ 23 GPa), our findings unambiguously demonstrate that this softening does not precipitate mechanical failure; rather, it signifies a transition to a dynamically flexible yet stable lattice configuration. The computed elastic stiffness tensors indicate that all doped systems adhere to the Born stability criterion, exhibiting positive stiffness eigenvalues, which confirms the mechanical stability of the structures despite diminished rigidity.⁷¹ Furthermore, phonon dispersion analysis shows that the soft modes introduced upon doping are localized in the low-frequency region and do not extend across the Brillouin zone, indicating the absence of global dynamical instability. These characteristics pertain to metastable anharmonic lattice flexibility rather than structural failure. Crucially, thermodynamic analysis derived from phonon simulations demonstrates a smooth and continuous progression of Helmholtz free energy, entropy, and heat capacity up to 1000 K, exhibiting no discontinuities or instability, thereby affirming the stability of the doped systems under realistic working conditions.⁷² This lattice softening is advantageous from a catalytic perspective, facilitating reversible structural adaptation during adsorption–desorption cycles, reducing reorganization energy, and improving electron–phonon coupling essential for effective CO_2 activation.⁷³ The Gd-doped system exhibits partial restoration of mechanical stiffness while maintaining superior catalytic performance, suggesting that an ideal equilibrium between lattice flexibility and structural integrity can be attained.

4 Conclusions

Lanthanide doping converts $\beta\text{-Ag}_2\text{Se}$ into a mechanically adaptable catalytic framework, wherein lattice softness, phonon dynamics, and metallic transport synergistically reduce CO_2

activation barriers. Elastic analysis reveals a significant alteration in lattice stiffness, as the bulk modulus diminishes from approximately 77 GPa in pristine Ag₂Se to around 23 GPa following La incorporation, before stabilizing at approximately 52 GPa for GdAg₂Se. This indicates a transition into a regulated soft-mode regime linked to low-frequency acoustic phonons and increased lattice polarizability. In this context, La primarily induces strong lattice softening and enhanced polarizability, facilitating structural flexibility and intermediate stabilization, whereas Gd provides a more balanced modification by combining controlled lattice softening with improved electronic conductivity and charge transfer competence. This mechanically softened yet stable environment for dynamic charge redistribution and structural adaptation of adsorbed CO₂, evidenced by a significant decrease in *COOH formation barriers from approximately 0.68–0.74 eV in Ag₂Se to around 0.28–0.63 eV in the doped systems. The presence of metallic carriers, controlled elastic anisotropy, and positive stiffness eigenvalues indicate that vibrational flexibility is attained without sacrificing structural integrity. Collectively, our findings indicate that dopant-engineered lattice softening is not simply a structural alteration but a functional process that aligns phonon-assisted relaxation with electron transfer to stabilize catalytic transition states. This combined elastic–electronic–kinetic framework establishes lanthanide-modified β-Ag₂Se as a paradigm system for the design of metallic catalysts, whereby regulated lattice adaptability directly improves reaction efficiency and longevity. These findings are directly relevant to applications in CO₂ electroreduction, thermoelectric-assisted catalysis, and integrated energy conversion systems, where efficient charge transport and dynamic catalytic adaptability are essential.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: other DFT characterization studies. See DOI: <https://doi.org/10.1039/d6cp00962j>.

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