

STRAIN-INDUCED STRUCTURAL TRANSITION IN BILAYER ZnS-8-16 POROUS NANOSHEETS: ROLE OF VIBRATIONAL STABILITY

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Received: 17 May 2026/ Accepted: 20 July 2026/ Published: 30 July 2026

<https://doi.org/10.70117/hdujs.E11.7.2026.1390>

Abstract: *This study proposes a novel bilayer ZnS-8-16 porous nanosheet and investigates its transition between cage-like (ZnS-8-16-C) and planar (ZnS-8-16-F) configurations. Using the DFTB+ method, phonon dispersion calculations reveal that the planar phase is dynamically stable, while the cage-like form exhibits vibrational instability. Under in-plane tensile loading, a structural phase transition from the cage-like to the planar configuration is observed. This geometric reconfiguration significantly modifies the electronic band structure, driving an indirect-to-direct band gap transition. Our findings highlight the role of vibrational stability in strain-induced transitions, providing a route for tuning the electronic properties of 2D porous ZnS systems.*

Keywords: *Bilayer ZnS-8-16, porous nanosheets, vibrational stability, strain-induced phase transition, electronic properties.*

1. Introduction

The rise of two-dimensional materials over the past two decades has opened up many new directions in materials science research. Owing to their atomic-scale thickness, these systems exhibit mechanical, electronic, and optical properties that differ markedly from those of their corresponding bulk phases [1]. Such unique characteristics have stimulated extensive efforts to explore two-dimensional materials for applications in nanoelectronics, sensing devices, and optoelectronic technologies [14,19].

In addition to dense two-dimensional structures, porous two-dimensional nanomaterials have recently attracted increasing attention [5]. The presence of periodically distributed pores not only enlarges the surface area but also significantly modifies the physical and functional properties of the materials [5,9]. As a result, porous two-dimensional nanostructures have demonstrated considerable potential for a wide range of applications, including energy storage, catalysis, and nanoelectronic devices [9,22].

Among semiconductor materials, ZnS has attracted considerable interest because of its wide band gap, high chemical stability, and favorable optical properties [25]. In addition to the well-known bulk phases, various low-dimensional ZnS structures have been proposed and investigated [11,16], indicating that structural modification can induce substantial changes in the electronic properties of the material.

In particular, the influence of mechanical strain on the electronic band structure of two-dimensional ZnS layers has been extensively studied, revealing that strain mainly leads to a continuous variation of the band-gap width within the same structural phase [6,8].

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However, these studies have not clarified the possibility of structural phase transitions between different geometric configurations under strain. Furthermore, existing investigations have focused primarily on monolayer systems [6,8] or dense structures [15], whereas bilayer porous nanostructures remain largely unexplored. Unlike continuous band-gap tuning observed in monolayer or dense ZnS [6,8,15], whether strain can trigger a structural phase transition in bilayer porous systems remains unexplored. Therefore, studying bilayer porous ZnS systems is necessary to gain deeper insight into their structural phase-transition behavior and the associated changes in electronic properties.

Vibrational stability is an important factor in evaluating the viability of material phases. Phonon spectra provide an effective means for this assessment: the presence of imaginary-frequency modes indicates vibrational instability, whereas a fully positive phonon spectrum is characteristic of a dynamically stable structure [21]. In many cases, structures that are vibrationally unstable exhibit greater sensitivity to external perturbations such as mechanical strain [13,24]. Consequently, vibrational stability may serve as a useful indicator for assessing both the existence and the structural phase-transition tendency of different configurations [13]. Nevertheless, the relationship between vibrational stability and structural phase transitions has not yet been systematically clarified across a wide range of materials, from bulk systems [13] to two-dimensional materials [7], and remains largely unexplored for bilayer porous nanostructures.

In this work, we propose a new bilayer porous ZnS nanosheet system and investigate two distinct configurations: a cage-like structure (ZnS-8-16-C) and a planar structure (ZnS-8-16-F). Using calculations within the DFTB+ framework, we analyze the vibrational stability of these structures and examine the relationship between vibrational stability and the structural phase-transition tendency between the two configurations. Under the investigated conditions, mechanical strain drives the cage-like structure toward the planar configuration, which exhibits higher vibrational stability. In addition, the geometric differences between the two structures lead to significant modifications in the electronic band structure. These findings suggest a correlation between vibrational stability and structural phase-transition behavior in the bilayer ZnS-8-16 system. Importantly, this work reveals for the first time that vibrational instability in the cage phase acts as a precursor for a strain-driven transition into a stable planar phase, accompanying an indirect-to-direct band-gap conversion. The results also reveal a close relationship between geometric structure and electronic properties, thereby indicating the possibility of tuning the band gap through structural phase transitions in this system.

2. Research Methodology

2.1. Structural Design Method

We propose a new two-dimensional polymorph of ZnS, constructed by combining eight-membered and four-membered rings within the framework of linking large-ring structural units [20,23], thereby forming an extended porous planar network. The basic repeating unit of the lattice, as illustrated in Fig. 1a, is a 16-atom ring-shaped pore. This pore is generated by connecting two eight-membered rings through three edge-sharing four-membered rings, giving rise to the characteristic in-plane {8-4-4-8} bonding topology.

While earlier porous architectures like nanoporous ZnO [23], twin 4–8 networks [20], or graphenylene-like ZnS [17,18] inherently retain hexagonal rings, our proposed ZnS-8-16 framework uniquely adopts a non-hexagonal {8-4-4-4-8} bonding topology with periodic 16-atom channels. The framework was then stacked in an AA'-type staggered arrangement along the direction normal to the plane, forming a bilayer system. We refer to this material as the 8-4-16 bilayer ZnS lattice (hereafter abbreviated as ZnS-8-16), a designation that reflects both its chemical composition and its ring-based topology. The optimized atomic structure is shown in Figs. 1a and 1b, corresponding to the side and top views, respectively. The resulting system may be regarded as a porous bilayer ZnS nanosheet characterized by an array of aligned periodic channels composed of 16-atom rings.

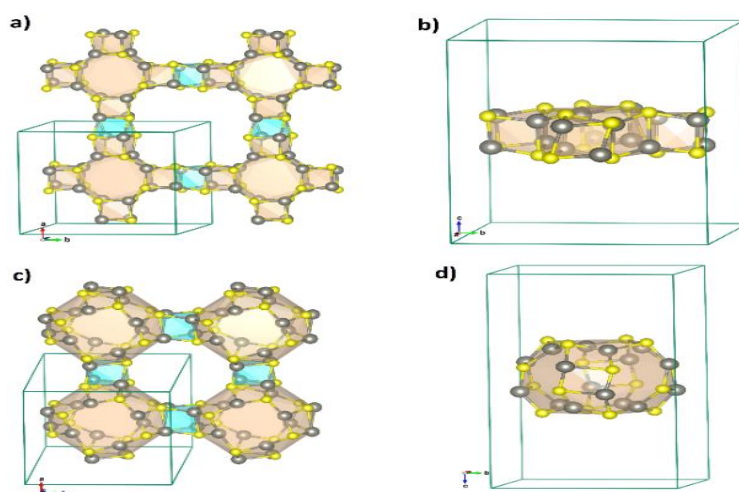


Figure 1. Structures of ZnS-8-16-F, shown in side view (a) and top view (b), and ZnS-8-16-C, shown in side view (c) and top view (d). The small yellow spheres represent sulfur atoms (S), the large gray spheres represent zinc atoms (Zn), and the blue frame indicates the unit cell.

To determine the equilibrium structure, we evaluated the dependence of the total energy on the in-plane lattice constant, during which an alternative nonplanar cage-like geometry was identified. This structure is denoted as cage-type ZnS-8-16 (hereafter abbreviated as ZnS-8-16-C), with the suffix “C” indicating the cage configuration. The corresponding structure is illustrated in Figs. 1c and 1d.

2.2. Density-Functional Tight-Binding Method

In this study, we employed the self-consistent charge density-functional tight-binding (SCC-DFTB) method, as implemented in the DFTB+ package [3,4]. The method is based on a second-order expansion of the total energy within density functional theory (DFT) with respect to charge-density fluctuations, offering an efficient description of large-scale material systems. SCC-DFTB uses the Znorg Slater–Koster parameter set to describe interactions between Zn and S atoms; this parameter set was derived from first-principles calculations. The theoretical foundation of the method, together with the parameterization procedure, has been presented in the original DFTB+ paper [3], its recent updates [4], and the references cited therein.

For simulations of the two-dimensional system, a vacuum region of at least 15 Å was introduced along the out-of-plane direction to eliminate interactions between periodic images. The Brillouin zone was sampled using a 5×5×1 Monkhorst–Pack k-point mesh. All structures were geometrically optimized until the force acting on each atom was less than 10⁻³ eV/Å.

3. Results and Discussion

3.1. Structural Characteristics

To clarify the structural characteristics of the bilayer ZnS-8-16 system, we analyzed the two configurations obtained after structural optimization, namely the planar structure (ZnS-8-16-F) and the cage-like structure (ZnS-8-16-C), as illustrated in Fig.1. Although both structures possess the same chemical composition and number of atoms in the unit cell (32 atoms), they exhibit pronounced differences in geometry and structural parameters, as summarized in Table 1.

In the ZnS-8-16-F structure, Zn and S atoms are arranged into a planar two-dimensional lattice containing periodic pores defined by 16-atom rings (Figs. 1a–b). The eight-membered and four-membered ring units are connected within the same plane, giving rise to a highly symmetric porous framework. In contrast, the ZnS-8-16-C structure exhibits an out-of-plane distortion of the lattice, leading to the formation of noncoplanar bonds and locally cage-like motifs (Figs. 1c–d).

The geometric differences between the two structures are further reflected in the calculated parameters listed in Table 1. In particular, the average Zn–S bond length in ZnS-8-16-F is approximately 2.4 Å, whereas it decreases to about 2.3 Å in ZnS-8-16-C, indicating distinct local bonding characteristics. At the same time, the average coordination number decreases from 3.5 in the planar structure to 3.0 in the cage-like structure, reflecting changes in the bonding environment around the atoms.

Table 1. Structural parameters of the two ZnS-8-16 configurations

Structures	ZnS-8-16-F	ZnS-8-16-C
Zn-S coord. Number	3.5	3
3D Crystal struct.	Tetragonal	Tetragonal
3D Symmetry groups	P422 (IT 89)	P422 (IT 89)
Unit cell (atoms)	32	32
Lat. param. (a;c) [Å]	12.44;15	10.27;20
Average Zn-S bond [Å]	2.4	2.3
Average angle (Zn-S-Zn/S-Zn-S)	94.1°/107.4°	97.2°/114.4°
Free Volume [Å ³]	1784.02	1544.51

Surface Area [$\text{\AA}^2$]	398.07	428.13
Cohesive energy/atom [eV]	3.86	3.81
Gap-type	Direct	Indirect
Band gap [eV]	2.28	3.13

In addition, the geometric distortion in the ZnS-8-16-C structure is further reflected in changes in the bond angles. In the planar structure, the average bond angles are approximately 94.1° and 107.4° , whereas in the cage-like structure these values increase to about 97.2° and 114.4° , indicating a greater degree of geometric distortion relative to the planar configuration.

Beyond the microscopic structural features, the macroscopic geometric parameters also exhibit significant differences between the two structures. ZnS-8-16-F possesses a larger unit-cell volume ($1784.02 \text{ \AA}^3$) than ZnS-8-16-C ($1544.51 \text{ \AA}^3$), while the cage-like structure exhibits a larger surface area ($428.13 \text{ \AA}^2$ compared with $398.07 \text{ \AA}^2$), reflecting differences in the porosity and morphology of the system.

From an energetic perspective, ZnS-8-16-F has a higher cohesive energy per atom (3.86 eV) than ZnS-8-16-C (3.81 eV), suggesting that the planar structure is energetically more favorable. However, the energy difference between the two structures is relatively small ($\sim 0.05 \text{ eV/atom}$), implying the possible existence of multiple geometric configurations under suitable conditions.

Overall, the ZnS-8-16-F and ZnS-8-16-C structures exhibit pronounced differences in their structural characteristics. Nevertheless, geometric and energetic analyses alone are insufficient to fully assess the stability of the system. Therefore, an investigation of vibrational stability through phonon spectra is necessary to clarify the nature of these structures, as discussed in the following section

3.2. Vibrational Stability of the Structures

Although the energy difference between ZnS-8-16-F and ZnS-8-16-C is relatively small, this information alone is insufficient to fully evaluate the stability of the system. Therefore, the vibrational stability of the two porous ZnS-8-16 structures was investigated through phonon calculations using the finite-displacement method, as implemented in the Phonopy package [2]. The obtained phonon spectra, including the phonon band structures and partial phonon density of states (PDOS), are presented in Fig. 2.

As shown in Fig. 2b, ZnS-8-16-F exhibits no imaginary-frequency modes throughout the entire Brillouin zone, indicating that this structure is vibrationally stable and corresponds to a true energy minimum on the potential-energy surface. All phonon branches remain within the positive-frequency region, reflecting a stable equilibrium state of the system in the planar configuration.

In contrast, ZnS-8-16-C exhibits imaginary-frequency modes in the low-frequency region (Fig. 2a), indicating that this structure is vibrationally unstable. The partial phonon density of states (PDOS) reveals that the low-frequency vibrational modes receive significant contributions from both Zn and S atoms. These results suggest that ZnS-8-16-C may be more sensitive to external perturbations than ZnS-8-16-F.

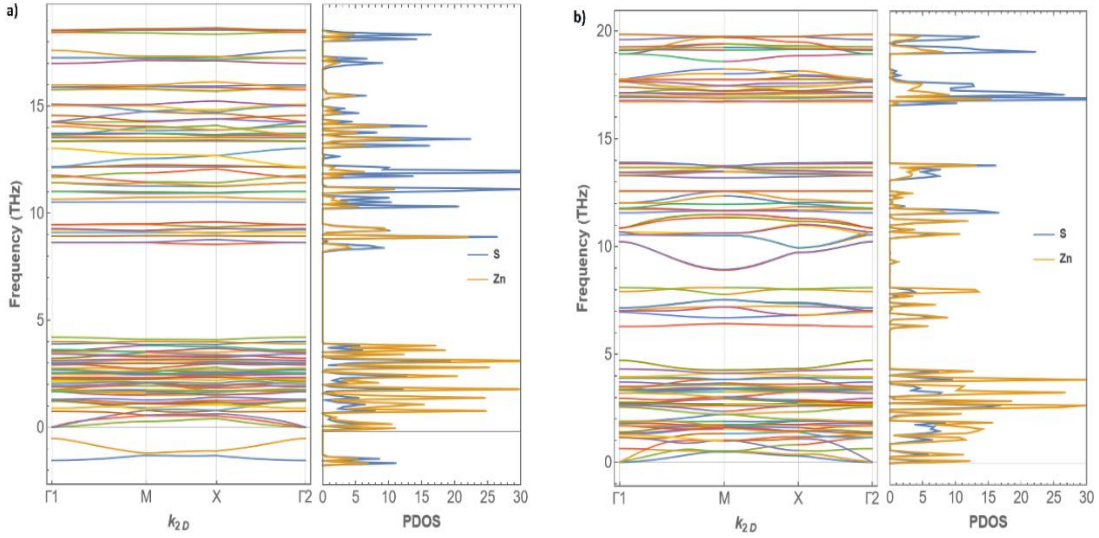


Figure 2. Phonon band structures and partial phonon density of states (PDOS) of ZnS-8-16-C (a) and ZnS-8-16-F (b)

Physically, imaginary phonon modes represent regions of negative curvature on the potential energy surface, indicating that the non-planar cage phase (ZnS-8-16-C) resides at an unstable saddle point [10]. Under in-plane tensile strain, the energy barrier separating the two configurations is significantly reduced, promoting atomic displacements along the soft mode eigenvector toward the dynamically stable planar phase (ZnS-8-16-F) [12]

Thus, the phonon analysis demonstrates that ZnS-8-16-F is vibrationally stable, whereas ZnS-8-16-C is vibrationally unstable due to the presence of imaginary-frequency modes. This result indicates that the cage-like structure is more susceptible to external perturbations than the planar structure. This interpretation will be further examined through simulations presented in Section 3.4.

3.3. Electronic Properties

To elucidate how structural differences affect the electronic properties of the system, we analyzed the electronic band structures and densities of states (DOS) for both the ZnS-8-16-F and ZnS-8-16-C phases. The calculated results reveal pronounced differences between the two structures in both the magnitude and the nature of the band gap.

Specifically, the planar ZnS-8-16-F phase exhibits a direct band gap of approximately 2.28 eV at the Γ point. In contrast, the cage-like ZnS-8-16-C phase possesses an indirect band gap of about 3.13 eV (Fig. 3), with its valence band maximum (VBM) located at the M point and its conduction band minimum (CBM) at the Γ point. These findings demonstrate that the structural transformation between the two phases modifies not only the magnitude of the band gap but also its character, driving an indirect-to-direct transition. The indirect-to-direct bandgap transition (3.13 eV to 2.28 eV) suggests that this material is highly suitable for optoelectronic devices, particularly for high-efficiency nano-LEDs and tunable optical switches operating in the visible range.

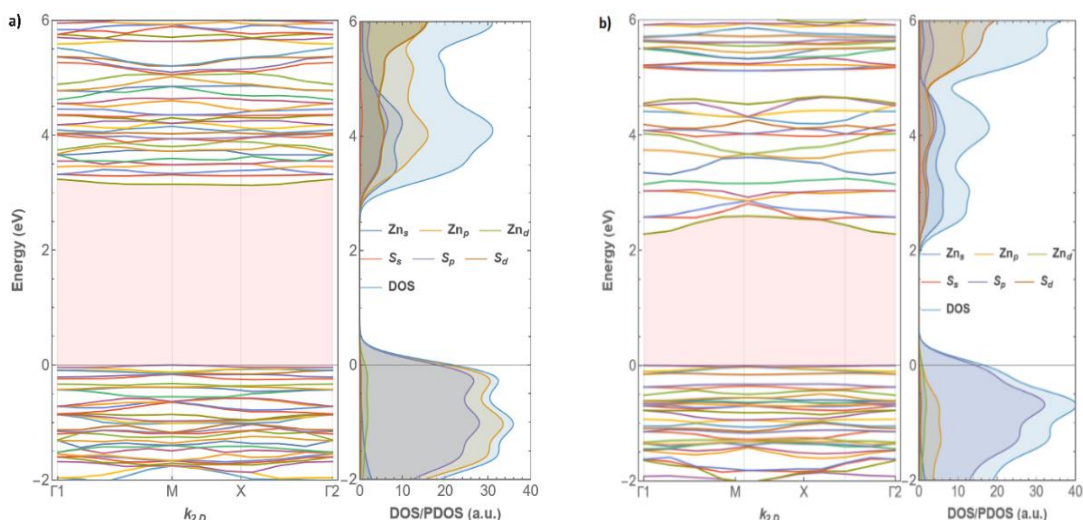


Figure 3. Electronic band structures, total density of states (DOS), and partial density of states (PDOS) of ZnS-8-16-C (a) and ZnS-8-16-F (b).

This variation can be correlated with the geometric differences between the two phases. As summarized in Table 1, the ZnS-8-16-F phase possesses a higher average coordination number than the ZnS-8-16-C phase, which contributes to enhanced orbital overlap and stronger effective electronic interactions within the plane. This effect may increase the dispersion of the energy bands near the band edges and consequently reduce the band-gap width. In contrast, the cage-like ZnS-8-16-C phase, characterized by a lower coordination number and a nonplanar geometry, may suppress orbital overlap and hybridization, resulting in less dispersive energy bands and a wider band gap. The behavior observed in this system is consistent with previous studies on cage-like and porous semiconductor systems, in which reduced orbital hybridization and enhanced electronic localization can lead to band-gap widening [17,26].

The partial density of states (PDOS) analysis indicates that the VBM is dominated primarily by the p states of S atoms, whereas the CBM mainly originates from the s states of Zn atoms in both phases. The differences in the electronic band structures are therefore likely associated with the distinct degrees of orbital overlap and the spatial distribution of the orbitals in the two configurations.

Combined with the vibrational-stability analysis presented in Section 3.2, these results indicate that structural differences not only alter the stability of the system but also lead to significant modifications in its electronic properties.

3.4. Structural Phase Transition under Tensile Strain

To investigate the effect of in-plane tensile stress on the structural evolution of the system, molecular dynamics simulations were performed in the NPT ensemble at a temperature of 300 K under an applied in-plane tensile stress of 0.5 GPa (corresponding to an external pressure setting of -0.5 GPa, where negative pressure specifies mechanical tension in NPT simulations). The simulations employed the Berendsen thermostat with a

time step of 1 femtosecond (fs) for 5000 simulation steps, corresponding to a total simulation time of 5 picoseconds (ps). Under the applied tensile stress, the in-plane lattice constant gradually increased over time, thereby driving the structural phase transition within the system.

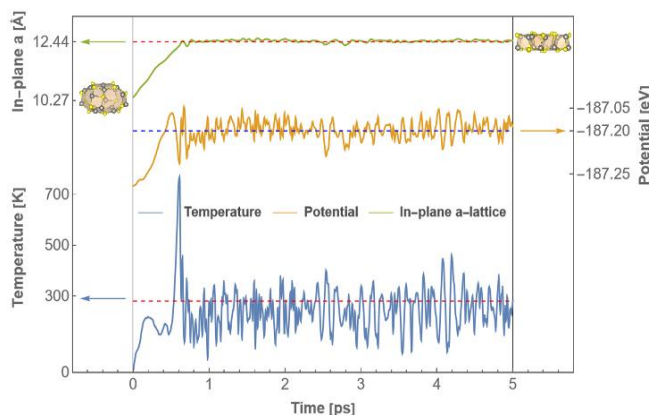


Figure 4. Molecular dynamics (NPT) simulation of the structural phase transition from ZnS-8-16-C structure (left) to ZnS-8-16-F structure (right) at 300 K under an in-plane tensile stress of 0.5 GPa.

The time evolution of the thermodynamic quantities is presented in Fig. 4. Specifically, the lattice constant a increases rapidly from approximately 10.27 Å to about 12.44 Å during the early stage of the simulation, accompanied by a pronounced variation in the potential energy. After approximately 0.6 ps, the system reaches a new stable state, with the relevant quantities fluctuating around their equilibrium values.

These structural and energetic variations directly reflect the stress-induced structural transition of the system. Examination of the corresponding atomic configurations indicates that the system evolves from the initial cage-like configuration (ZnS-8-16-C) to the planar configuration (ZnS-8-16-F), a process accompanied by subtle adjustments in the bond lengths and bond angles within the crystal lattice.

These results suggest that tensile strain can act as an external driving force for the structural phase transition from the cage-like to the planar configuration. This observation is consistent with the vibrational-stability analysis presented in Section 3.2, in which the cage-like structure was identified as vibrationally unstable and therefore more susceptible to external perturbations than its planar counterpart. While the 5 ps simulation timeframe is sufficient to capture this ultrafast, soft-mode-driven structural reconfiguration under the specific stress condition, further studies with varied strain paths and longer timescales will be helpful to fully map the transformation kinetics.

4. Conclusion

In this study, we investigated the structural characteristics, vibrational stability, and electronic properties of bilayer porous ZnS-8-16 nanosheets in both planar and cage-like configurations using the DFTB+ method. The results show that the planar structure is vibrationally stable, whereas the cage-like structure is vibrationally unstable due to the presence of imaginary-frequency modes.

The structural differences between the two phases are accompanied by pronounced differences in their electronic properties. In particular, the planar structure exhibits a smaller direct band gap, while the cage-like structure possesses a larger indirect band gap.

Molecular dynamics simulations further reveal that, under tensile strain, the system tends to transform from the cage-like structure to the planar configuration. These findings indicate that, in the bilayer ZnS-8-16 system, vibrational stability is closely related to the tendency for structural phase transitions between the investigated configurations. These findings also highlight the potential for tailoring material properties through the targeted selection of structural configurations. Furthermore, the strain-dependent modulation of the electronic band structure indicates possible opportunities for band-gap tuning, which may offer useful theoretical guidelines for the future design of low-dimensional optoelectronic and sensing devices

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Acknowledgment. We would like to thank the referee for careful reading of the manuscript. The referee's comments, remarks, corrections, and suggestions have significantly improved the quality of this paper. This research is funded by Hong Duc University under grant number DT-2025-05.