Electronic structures of ZnX (X = O and S) nanosheets from first-principles energy loss near edge structure studies

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This paper tries to study the core energy loss spectra of zinc based nanosheets (ZnO and ZnS) in density functional theory using the FPLAPW method. We have calculated the energy loss near edge structure (ELNES) spectra of zinc K- and L2,3-edges, and oxygen and sulfur K-edges in ZnO and ZnS nanosheets at magic angle conditions and compare to those of ZnO and ZnS wurzite bulk structures. As a result of the smaller bond lengths in the nanosheet structures, all the ELNES spectra in nanosheets, including Zn K- and L2,3-edges, and O and S K-edges show a shift to the higher energies. The calculations reveal that in comparison to ZnO structures, all the ELNES spectra of ZnS structures including the bulk and sheet show a shift to lower energy region. This is a result of larger bond lengths in ZnS structures, and that it can be used to fingerprint each structure. The comparison of ELNES spectra and unoccupied symmetry-projected density of states (local DOS) confirms that Zn K-edges of both ZnO and ZnS nanosheets have main features including the electron transition to $\pi^*$ and $\sigma^*$ states which this is a sign of the strong sp$^2$ hybridization and it is absent in Zn K-edge of ZnO and ZnS bulks. Moreover, in comparison to bulks, the energy differences between some main features in Zn based nanosheets decreases. The accordance of ELNES spectra and unoccupied local DOS shows that the main contributions in Zn L-edges ELNES of ZnO and ZnS nanosheets refer to transitions to mostly d-symmetry states and p-d hybridization. Orientation dependencies of the spectral features in nanosheet structures were also considerable. The overall dispersions of oxygen and sulfur K-edges in bulks and nanosheets are different. Since the inclusion of core-holes and super-cells is essential for accurate reproduction of features in ZnO and ZnS bulks and due to the rather wide band gaps of Zn based nanosheets, it may be essential as well for all the ELNES spectra of nanosheet structures.

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1. Introduction

Of the important semiconductors are zinc based materials [1–3] which are promising compounds in direct and potential electronic and optoelectronic applications. Zinc oxide (ZnO) is a prototypical II-VI wide band gap semiconductor [4]. Due to its electronic, thermal and optical properties such as high reflectivity index [5,6] and high thermal conductivity [7], pure and doped ZnO structures have direct industrial applications in the laser diodes, light emitting diodes, solar cells, ultraviolet diodes, electroluminescent panels and the other optoelectronics applications [8].

Quick progresses in the nanotechnology science have led to synthesize and produce low-dimensional and nano based materials such as nanotubes, nanobelts, nanorods, nanowires and nanosheets, and their wide usage in the electronic and optoelectronics devices [9–15]. Of these, the sheet structures have attracted wide attentions due to the large and sensible changes in physical and chemical properties of materials for going from the bulk to the surface [16–22]. ZnO and ZnS nanosheet (ZnX-NS) structures, the graphene-like monolayers, are included in these categories. They have many applications in lasers, sensors, and the infrared and luminescence sensitive devices [23,24]. They have intensely been the topics of many areas of chemical and physical studies. Recently, electronic and optical properties of pure and doped ZnO-NS have been studied. Al- and In-doped ZnO-NS show half-metallic character, leading to an n-type semiconductor [25]. The doped ZnO nanosheet with some Zn site substituted atoms with Co atoms tends to form a ferromagnetic treatment [26]. Under a tensile strain, a direct to indirect band gap transition has theoretically been predicted for ZnS monolayer, enabling to use in the straintronics applications [27].

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It will be interesting to study the local electronic structures of ZnO- and ZnS-NS in an accurate method and compare with the corresponding in the bulk of wurtzite ZnO and ZnS (ZnX-B). Energy loss near edge structure (ELNES) is a technical method, giving this possibility [28]. It is a high resolution technique, detecting the fine structure, sensitive to the chemical bonding and the atomic arrangements in different classes of materials. This originates from the transition of a core electron to unoccupied states, reflecting the partial density of states of unoccupied bands. Electronic structures of ZnO- and ZnS-B have theoretically been studied [29,30], but there is not any study around the local electronic structures of ZnO- and ZnS-NS by means of the near edge structure analysis. In this study, we have dealt with the core loss spectra of Zn based nanosheets on the basis of the full potential linearized augmented plane wave (FLAPAW) method implemented in the all electron code, WIEN2k [31]. By means of some approximations, WIEN2k code successfully finds reasonable results for the ELNES spectra [32]. Its prosperities and successes have been affirmed by several studies around the ELNES spectra of dissimilar classes of materials, obtained by WIEN2k. For example, one can see Refs. [33-35].

This paper has been organized as follow. After describing the ab initio calculation method, electronic structures of bulk and sheet ZnX structures are discussed. Theoretical estimations for the effect of sheeting on the structural and electrical properties of ZnX structure are presented. Then, electron energy loss near edge structures of ZnX monolayers are calculated and discussed and a by means of the analysis of different edge structures, a comparison between local electronic structures of bulk and nanosheets and also of Zn edges in different sheets is made. Due to the instrumental limitation to experimentally measure the spectra higher than 3 keV using EELS, in order to check our results the computational ELNES spectra were compared with the existing experimental ELNES or XANES spectra.

2. Computational details

2.1. Computational parameters

The present calculations are based on the all electron full potential method, FLAPAW. The structural and electronic properties have been done relativistically. In solving Kohn–Sham equations, the exchange-correlation potential was calculated by means of the Perdew–Burke–Ernzerhof (PBE) scheme of the generalized gradient approximation functional (GGA) [36]. The cutoff vector in expanding the wavefunctions in the interstitial region, \( k_{\text{max}} \), was chosen in a way that converging \( k_{\text{MT}} \approx 4k_{\text{max}} \) of total energy, electron charge density and energy loss spectra equals 7. The maximum quantum number for the wavefunction expansion inside the atomic sphere was confined to \( k_{\text{max}} = 10 \). The \( k_{\text{max}} \) parameter was taken to be 12 Bohr \(^{-1}\). Brillouin zone (BZ) integrations within self-consistency cycles were performed via a tetrahedron method containing 16 (7 \( \times \) 7 \( \times \) 3) and 12 (9 \( \times \) 9 \( \times \) 1) \( k \)-points in the irreducible BZ of the ZnX-B and ZnX-NS, respectively. Crystal lattices and atomic positions of ZnX-B and ZnX-NS are fully optimized up to the residual force on every atom be less than 0.5 mRyd/a.u. In order to neglect any interlayer interactions, we set the optimized distance 10 Å between ZnX layers.

2.2. The ELNES spectra method

In the band structure method, the ELNES is calculated within the first Born approximation with the assumption that the incoming and outcoming fast electrons are plane waves with wave vectors \( k_i \) and \( k_f \). The double differential scattering cross section (DDCS) for the inelastic electron scattering is given by [37]:

\[
\frac{d^2\sigma}{d\Omega dE}(E, q) = \left[ \frac{2\gamma}{\epsilon_0 q^4} \right] \frac{k_i}{k_f} \sum_i |\langle f|e^{i\hat{r}}|i\rangle|^2 \delta(E - E_f + E_i)
\]

where \( q = k_i - k_f \) is the momentum transfer, \( q_0 \) is the Bohr radius, \( E \) is the energy loss, and \( \gamma = \sqrt{1 - \frac{4}{x^2}} \) is the relativistic factor. The summation is done over all occupied initial and unoccupied final one-electron states. The initial state is the ground state of the target electron and the final state is the state occupied by the target electron in the conduction band after interaction. Eq. (1) can be recast in terms of the unoccupied density of states, \( \chi(E) \). With some approximation [38], we can write:

\[
\frac{d^2\sigma}{d\Omega dE}(E, q) = \sum_{lp} |M_{lp}(E, q)|^2 \chi_p(E)
\]

which is a sum of transitions to final states of \( l_p \)-character (s, p, d, . . .). \( M_{lp}(q, E) \) is a smooth and slowly decaying function of energy loss, representing the overall shape of the edge, in a way that variations in DDCS represent the energy dependence of the densities of states (DOS) above the Fermi level. To simulate the energy loss near the edge structure, we used the TELNES3 program [31], a modified version of TELNES, which involves the fully relativistic effects, and which is a part of the WIEN2k program. Since the core-hole left by the excited electron locally changes the potential, and therefore, influencing the electron density, it serves as a perturbation, so the valence and conduction states can be contracted and shifted. The projected density of states is changed, and the overall shape of the spectrum can be strongly modified, in a way that it may even lead to excitonic peaks in the ELNES. The core-hole calculations, giving these modifications, have been carried out by the reduction of the occupancy of the core level corresponding to the observed edge. In order to avoid renormalization problems, the missing charge is added to the unit cell as a uniform background charge. To avoid the interaction among neighboring core-holes, we used super-cell structures. This approach including the DFT, the super-cell, and the core-hole, namely, “Final State Rule” (FSR) [39], was used for all spectra. This rule states that the calculation is done via Fermi’s golden rule with final states being calculated with a final state Hamiltonian including an appropriately screened core-hole, while the initial states should be those for the ground state. We used 108 (3 \( \times \) 3 \( \times \) 3), and 50 (5 \( \times \) 5 \( \times \) 1) atoms (dimensions of super-cells) for the bulk and nanosheet super-cell structures, respectively, to avoid the interaction among neighboring core-holes. These sizes of super-cells have been optimized up to the results of the spectra without changes. The calculated ELNES must be broadened before being compared to the experiments. Thus, we performed an energy-dependent broadening on the spectra with a linear Lorentzian function \( \Gamma = 0.1E \), originating from the excited states lifetime.

3. Results and discussion

ZnO (ZnS) sheet is a monolayer structure constituted of Zn and O (S) atoms with the strong sp\(^2\) hybridization in a graphene-like plane. Fig. 1 gives a schematic view of ZnX-B and ZnX-NS. With increasing the lattice parameter \( c \) in the \( z \)-direction, the interaction among atoms in the bulk tends to be minimized and then the wurtzite lattice is changed to a planar graphene-like structure. In the wurtzite crystal structure, the coordination number of Zn and X atoms is 4 (sp\(^3\) hybridization), while in the nanosheet it decreases to 3 (sp\(^2\) hybridization). In a honeycomb lattice, each Zn atom connects to the three oxygen (sulfur) atoms. In our calculations, at first we consider a three-dimensional wurtzite bulk ZnO (ZnS) structure.
in which all the atoms are fourfold coordinated through hexagonal directed sp$^3$ orbital. After optimization, the hexagonal lattice constants under equilibrium are $a = b = 3.292$ (3.820)Å, $c = 5.220$ (6.260)Å, which are used for constructing the nanostructures. Next by means of wurtzite ZnO (ZnS) crystal structures, we studied two-dimensional nanosheets. Increasing the interatomic distance, $c$, led to transform the pristine ZnO and ZnS from the initial configuration (Fig. 1 (top)) to a flat graphene-like structure (Fig. 1 (bottom)). For the structural optimization, the energetic convergence threshold is $10^{-4}$ Ry. Atomic relaxation is carried out until all components of the residual forces are less than 1 mRy/Å. This results in a pronounced geometry change in which the lattice parameters of two dimensional ZnO (ZnS) were obtained $a = b = 3.328$ (3.870)Å and the length of Zn-O (Zn-S) bond has changed from 1.925 (2.257) to 1.921 (2.234)Å. Moreover, the bond angle within the newly formed planar layer increases from the wurtzite tetrahedral, 109°, to plane trigonal, 120°. These values are in agreement with the theoretical and experimental reports for bulks and nanosheets [40–42].

Although there are different studies on the energy gap of ZnO-B and ZnO-NS, the lack of an exact calculation of energy gap of ZnS-NS reveals the need for specifying its energy gap through a precise method. Therefore, the many body $G_0W_0$ approximation [43] implemented in exciting-code [44] was used to calculate the exact value of ZnS-NS band gap. Fig. 2 represents band structures of bulks and sheets of ZnX structures, calculated in the one-particle GGA-PBE, compared to ZnS-NS band gap in many-body $G_0W_0$ approximation. In the case of ZnO, the energy band gaps and the dispersion of bands are in agreements with the other theoretical reports [40]. ZnO (ZnS) in hexagonal wurtzite crystal structure is reported to be a direct gap semiconductor 3.37 (3.91) eV [8,29]. Its band gap in GGA was obtained equal to 0.95 (2.05). In GGA approximation, the energy band gaps of ZnO- and ZnS-NS were obtained 1.66 and 2.57 eV, respectively. To our knowledge, there is no study for the GW band gap of ZnS-NS. Its band gap in $G_0W_0$ approximation was obtained 5.83 eV which it is larger than 2.57 of KS-PBE (Fig. 2). The difference between computational and experimental results refers to the well-known underestimation of GGA approximation.

However, ZnX-B and ZnX-NS are wide band gap semiconductors. In the bulk, hybridization is sp$^3$ while it is changed to sp$^2$ in the graphene-like structures, causing the valence and conduction

**Fig. 1.** Bulk (top) and nanosheet (bottom) structures of ZnX (X = O and S) in side (left) and top (right) views. Zinc atoms are blue and X (oxygen or sulfur) atoms are yellow spheres.

**Fig. 2.** Band structures of bulk (left) and nanosheet (right) of ZnO (top) and ZnS (bottom) in KS-GGA (black solid line) and many-body $G_0W_0$ approximation (red dashed line).
bands to be near. Therefore, ZnX-NS can exhibit very different electronic properties, as compared with the bulk.

Afterwards, within the GGA approximation, using a 300 keV electron beam, we calculated the energy loss spectra in ZnX-B and -NS. This includes Zn K- and L_{2,3}-edge in the both bulk and sheet of ZnO and ZnS and also O and S K-edge in these structures. For all the spectra, the results were obtained by specifying the magic angle value, the collection angle giving the orientation resolved spectrum. Supplied with TELNES3, the magic angles for all the spectra were specified by means of calculating the ratio of out-of-plane and in-plane contributions of spectra for the three sample-to-beam orientations. The magic angle occurs at the cross of three curves, as for Zn K-edge it has been displayed at Fig. 3(a). As Fig. 3(b) shows, the calculated Zn K ELNES in ZnO-NS at the magic angle (23.57 mrad) has no changes for the three sample-to-beam orientations, 0, 45 and 90 degrees. The magic angles for Zn K (L_{2,3}) edges in ZnO-NS and ZnS-NS were obtained equal to 23.57 (2.57) and 21.60 (2.35)mrad, respectively. The corresponding values for O and S K-edges are 1.24 and 5.54 mrad, respectively. In the case of ZnO-NS and ZnS-NS, structures, magic angles for Zn K (L_{2,3}) edges were obtained 21.84 (2.38) and 21.8 (2.38)mrad, respectively, and 1.23 and 5.50 mrad for O and S K-edges. In addition, in order to get the precise results, the effect of the hole left by the electron transition was included by means of applying the core-hole approximation within different sizes of super-cells up to the convergence of the results. The results of ELNES calculations are discussed below:

### 3.1. ZnO

#### 3.1.1. Zn K edge

Compared with the experiment [45], Zn K-edge spectrum in ZnO bulk has been shown in Fig. 4. Our result and the experimental spectrum are in an excellent agreement, showing the precision of our calculations. The main features are well reproduced, including the peaks labeled by A, B1, B2, C and D in the experimental spectrum. Due to the wurtzite crystal structure with the hexagonal basis, ELNES and XANES spectra of ZnO show high anisotropy and therefore the orientation dependency. In the experimental ELNES, the labeling of peak B refers to these orientation dependent measurements. Mizoguchi et al. [45] measured the Zn K ELNES/XANES in ZnO with an averaging on the spectra obtained by the electron beam descended on the in-plane and out-of-plane orientations. In addition, using polarized X-rays of which the electric field is either parallel or perpendicular to the c axis, Mizoguchi et al. [45] measured and calculated the XANES spectrum of ZnO that can be implicitly compared with the ELNES spectrum. They attributed peak B_2 to the parallel component to the c axis (out-of-plane), whereas peak B_1 has been attributed to the perpendicular component to the c axis (in-plane). Since we have calculated the ELNES spectrum at the magic angle, this orientation dependency has been rectified and Zn K ELNES is orientation independent.

When a core-hole is created due to the excitation of a core electron, valence electrons move, and they screen the core-hole potential. In metals, the valence electrons can move easily, so the core-hole effect would be less significant, whereas in semiconductors and insulators, the electrons cannot move easily because of the filled valence band, and therefore, the core-hole effect would contribute significantly to the unoccupied DOS. Since the bulk and sheets of both ZnO and ZnS structures are wide band gap semiconductors, the screening effect on the core-hole by the valence electrons is weak. Due to the selection of large size super-cells in order to neglect the interaction between neighboring core-holes, and due to the large energy gaps, ELNES/XANES spectra are different in the ground state cells and super-cells. Fig. 4 represents the ELNES/XANES spectra of Zn K-edges in the wurtzite ZnX bulks and nanosheets, calculated in the converged super-cells. In all the spectra, the edge onsets have been set to zero (dotted lines) by the shifts equal to the required energy to remove the core electrons of the corresponding atoms, so that the suitable comparisons can be made. Despite the existence of equivalent peaks in K-edge of ZnO nanosheet compared to that of ZnO bulk, one can see the slight changes in the overall dispersion of ZnO nanosheet spectrum. These changes are in the energy difference between peaks B and D, and in the overall dispersion of edges at the first 10 eV beyond the onset. In ZnO bulk, peaks labeled by A, B, C and D have occurred at 6.32, 10.58, 14.44 and 22.08 eV, respectively. The corresponding peaks in the nanosheet are at 6.5, 10.75, 13.05 and 19.65 eV, respectively. In the bulk and nanosheet, the energy differences between peaks B and D are 11.5 and 8.9 eV, respectively. Compared to the corresponding peak in the bulk, peak A in the nanosheet shows a shift to the higher energy region. In addition, there is a shoulder labeled by A’ in the nanosheet at 4.2 eV that it has not been appeared in the bulk. The pointed differences indicate that the bindings are changed in the layering of ZnO. In the bulk, each zinc atom is connected to four oxygen atoms with sp^3 hybridization, while in nanosheet, each zinc atom is connected to three oxygen atoms and therefore the hybridization must apparently be changed from sp^2 to sp^3. In wurtzite ZnO (ZnS) structure, atoms are four fold coordinated through tetrahedrally directed sp^3 orbitals, whereas the atoms in two-dimensional graphene-like ZnO are three fold coordinated through sp^2 orbitals. Since sp^2 bonding in ZnO (ZnS) nanosheet is stronger than the tetrahedrally coordinated sp^3 bonding in the three-dimensional wurtzite structure, the bond length of Zn–O (Zn–S) in the graphene-like ZnO (ZnS) honeycomb structure is smaller than that in the bulk crystals. These are in agreement with Topaksal et al. work [40].

Due to the smoothly varying of matrix elements in Eq. (1) with respect to the energy, in the frame of dipole selection rules, the origins of ELNES structures can be revealed by means of the unoccupied symmetry-projected density of states of the excited atom, i.e., local DOS. Fig. 5 compares the unoccupied local densities of states of ZnX in the bulk and nanosheet structures, which directly
Fig. 4. Left panels: (a) The experimental ELNES spectrum of Zn K-edge in ZnO bulk [45], and calculated Zn K-edges in (b) bulk and (c) sheet of ZnO. Right panels: (d) Experimental XANES spectrum of Zn K-edge in ZnS bulk [52], and calculated Zn K-edges in (e) bulk and (f) sheet of ZnS.

Fig. 5. Left panels: unoccupied $p$-DOS of zinc atom in (a) bulk and (b) sheet of ZnO. Right panels: unoccupied $p$-DOS of zinc atom in (c) bulk and (d) sheet of ZnS.
interpret the ELNES spectra. Obviously, a comparison between Fig. 4 and Fig. 5 indicates that the overall dispersions of the local DOS are similar to those of the ELNES spectra. This means that the main peaks in ELNES spectra are related to the main peaks in the local DOS. Zn p-DOS in ZnO bulk (Fig. 5(a)) shows a shoulder at 6.33 eV and a strong peak at 10.82 eV, corresponding to shoulder A and peak B in Zn K-edge in ZnO, respectively. The structures occurred at 14.38 and 22.25 eV in p-DOS of Zn atom correspond to peaks C and D in Zn K-edge. At the energy positions of shoulder A and peak B, the main contributions of p-DOS of Zn originate from $\sigma (p_{xy})$ states. Therefore, shoulder A and peak B in Zn K-edge of ZnO bulk refer to electron transition to mostly $\sigma (p_{xy})$ states. In fact, due to the tetrahedral symmetry of ZnO (ZnS), the transition of 1s electron to $p_{xy}$ states has the main contribution in the Zn K-edge. The pre-edge at the onset (A) can be attributed to 1s electron transition to mostly $4p_z$ states and the main peak labeled by B can be assigned to the 1s electron transition to $4p_x$ and $4p_y$ states. This is confirmed by the Zn K edge studied by Lee et al. [46]. In addition, Fig. 5 (a) shows that the contribution of $p_z$ states in the feature labeled by C in Zn K-edge is considerable. Despite the existing of both $\pi (p_z)$ and $\sigma (p_{xy})$ states at the energy position of peak D, this peak in Zn K-edge originates from the mostly $\sigma (p_{xy})$ states. In addition to the local DOS, a second tool for interpreting the ELNES assignments is the ELNES/XANES decomposition to its $(l', m')$ components. Fig. 6 depicts this decomposition for the bulks and nanosheets of ZnO and ZnS. In Fig. 6 (a), it is obvious that the out-of-plane component $(l = 1, m' = 0)$ of Zn K edge contributes mainly to the first (A) and third (C) peaks, whereas the in-plane $(l' = 1, m' = \pm 1)$ element has the main role in the second (B) and forth (D) features.

Compared to ZnO bulk, one can see some differences in the p-DOS of zinc atom in ZnO nanosheet (Fig. 5 (b)). The first peak in p-DOS of zinc atom in ZnO nanosheet has mostly $p_z$ symmetry whereas the others have mostly $p_{xy}$ symmetries. This is obviously a sign of the $sp^2$ hybridization similar to which is observed in the carbon K-edge in graphite, i.e. a $\pi$ peak at the onset and the excitation peak $\sigma'$ at higher energies [47]. There is hybridization of $\pi (p_z)$ and $\sigma (p_{xy})$ states at 4.24 eV, the peak position of the A' structure. Therefore, shoulder A' in Zn K-edge of ZnO nanosheet can be attributed to this hybridization. The latter peaks in p-DOS of ZnO, occurred at 6.85 and 10.80 eV are constructed of mostly $\sigma (p_{xy})$ states. Therefore, peaks A and B in Zn K-edge are due to transition to mostly $\sigma (p_{xy})$ states. The C structure is more shoulder like and it includes mostly $\sigma (p_{xy})$ states. Another peak at 19.78 eV in p-DOS confirms that in Zn K-edge of ZnO nanosheet, the intense peak labeled by D can be attributed to transition to mostly $\sigma (p_{xy})$ states. Zn K edge ELNES/XANES decomposition to its components for ZnO monolayer is displayed in Fig. 6 (b). This shows that the first peak originates from 1s electron transition to mostly $\pi$ states whereas $\sigma$ states play the main role in the other parts of the spectrum up to 27 eV beyond the edge inset. As pointed above, this behavior is a characteristic trait of the existence of sp$^2$ hybridization [47,48].

### 3.1.2. Zn L$_{2,3}$ edge

Fig. 7(b) and (c) shows the calculated Zn L$_{2,3}$-edges of ZnO in bulk and sheet structures, respectively. The calculated ELNES of bulk is in a good agreement with the experimental work by Mizoguchi et al. [49] displayed at Fig. 7(a). In Zn L-edge spectra of bulk and nanosheet, the main features are somewhat different. The origins of these structures can be clarified by means of describing the unoccupied DOS. Fig. 8(a) and (b) show the unoccupied partial DOS of excited Zn atom in the bulk and nanosheet of ZnO, respectively. At the frame of dipole transitions, Zn L$_{2,3}$-edge spectrum corresponds to the excitation of 2p-electron to the unoccupied Zn $s$- and d-like states. An amazing accordance between L-edge and the unoccupied d-DOS of ZnO bulk (Fig. 8 (a3)) demonstrates that in Zn L-edge, the main contribution of transitions refers to d-states. In addition to the edge onset, s-states of Zn atom have some contributions at 20 eV beyond the onset. Fig. 8(a2) displays the different contributions of d-components in the DOS of ZnO bulk. Therefore, a shoulder at 5.41 eV and a peak at 7.38 eV can be attributed to $e_g (d_{xy})$ and $e_g + t_{2g} (d_{xz}, d_{yz})$ symmetries, and the hybridization of $e_g (d_{xz})$, $e_g + t_{2g} (d_{xy}, d_{yz})$ and $t_{2g} (d_{xy}, d_{yz})$ symmetries, respectively. There are two broader peaks at 10.91 and 12.08 eV in L-edge of bulk which the former can be assigned to a hybridization of $p$- and d-state, and the latter to $t_{2g} (d_{xz}, d_{yz})$ states. It is found that peaks A and B of the wurtzite compounds are composed of both cation $s$ and cation $d$ orbitals. Since atoms in the wurtzite structure have tetrahedral coordination, when an isolated atom in these crystals is assumed, the p–d hybridization is allowed in the wurtzite structure. In these crystals, cations and anions are bonded with each other and these orbitals are broadened. Due to the presence of the p–d hybridization, the degree of the band dispersion of the d orbital is expected to be broad in wurtzite structure. The broader p–d orbitals can therefore contribute to the peaks on the lower energy side of L$_{2,3}$ edge in the wurtzite compounds.

In the case of ZnO nanosheet, there is a large accordance between Zn L-edge and d-DOS (Fig. 8 (b1,2)). This indicates that like the bulk, the structures beyond the first 10 eV in Zn L$_{2,3}$-edge of ZnO nanosheet originate from transitions to d-states of Zn atom. At the energy position of the first shoulder, s- and $e_g (d_{xz})$ states have the main role in the transitions. The first peak at the energy position 6.58 eV can attributed to $e_g + t_{2g} (d_{xz}, d_{yz})$ and mostly s symmetries and the second one at 8.40 eV can be attributed to equal contributions of both s and d symmetries. At the energy range of 10 to 18 eV, one can assign the structures in Zn L-edge to mostly $t_{2g}$ symmetry. In addition, the structures above 18 eV can be attributed to both $e_g$ and $t_{2g}$ states.

### 3.1.3. O K edge

Now, we deal with O K-edge spectrum in ZnO. Like the other ELNES spectra discussed in this paper, in order to get the best accordance with the experiment, including the effect of core-hole left by the excited electron is mandatory. For attaining this accordance, the use of a 108 atom super-cell with $3 \times 3 \times 3$ dimensions seems to be sufficient. As Fig. 9 indicates, the calculated O K-edge in ZnO bulk has an excellent agreement with the experimental spectrum.
reported by Mizoguchi et al. [45], and the other experimental result [50], indicating the reliability of our calculations. The first feature (A) is a shoulder-like structure occurred at 4.85 eV and the second one (B) is a peak occurred at 6.7 eV. These two features have origins associated to transition of 1s electron to mostly $\sigma'$ ($p_{z\gamma}$) states (Fig. 10 (a)). There are two broader features, namely C and D, occurred at 10.54 and 12.4 eV, respectively. Fig. 10 (a) attributes them to mostly $\sigma''$ states, although the contribution of $p_z$ states is not negligible. Peak E occurred at 25.1 eV can be assigned to transition to $\sigma''$ state.

Compared to the bulk, O K-edge of ZnO nanosheet has a shift to the lower energy region (Fig. 9 (c)). The contribution of $\pi$ state in the first peak is considerable. In addition, the energy difference between peaks A and B decreases from 1.85 in bulk to 0.98 eV in nanosheet, which can be concerned to the smaller Zn–O bond length in latter. The ELNES spectra are highly sensitive to the bond lengths in the structures. For example one can see the comparison of carbon K edge ELNES spectra of diamond, graphite and carbon amorphous studied by J. T. Tittanah and D. Lamoen [51]. Features C, D and the broader one, E have occurred at 6.3, 11.82 and 21.3 eV, respectively, which can be attributed to transition to mostly $\sigma$ states. Altogether, the broadening of O K-edge in nanosheet is lower than that of bulk.

3.2. ZnS

3.2.1. Zn K edge

Fig. 4 shows the calculated Zn K-edge in ZnS bulk. Compared to the experimental XANES [52], the main ELNES features have been well reproduced. In the case of Zn K-edge in ZnS, the dispersions of ELNES spectra are intensely different in the bulk and nanosheet (Fig. 4(e) and (f)). The main structures in the bulk are a strong peak at 5.24 eV, labeled by A, and two broader peaks at 15.04 and 18.86 eV, labeled by B and C, respectively. In the nanosheet, the main structures are peaks occurred at 5.42 (A), 8.74 (B) and 12.16 (C) eV, and a broader one occurred at 19.98 (D) eV. As in the case of ZnO, the first peak in ZnS nanosheet has a shift to higher energies compared to the first peak in ZnS bulk, which can be assigned to the smaller bond length in the nanosheet. Compared to bulk, Zn K-edge in nanosheet has a smoother decrease at higher energies.

Fig. 5(c) displays p-DOS of the excited Zn atom in ZnS bulk. A comparison to Fig. 4(c) can appears the origin of ELNES structures of bulk. Peak A can be attributed to mostly $\sigma'$ ($p_{x\gamma}$) states. This behavior is confirmed for peaks labeled by B and C. In the case of nanosheet, some differences are observable (Fig. 5(d)). Peak A in ZnS nanosheet is due to transition to mostly unoccupied states of $\pi^*$ ($p_z$) symmetry and the other features can be attributed to $\sigma'$ ($p_{x\gamma}$) states. Like ZnO nanosheet, this introduces a $sp^2$-coordinated zinc atom, like the carbon atom in the graphite structure. In addition, at energy 3.2 eV in p-DOS, there is a hybridization of $\pi$ ($p_z$) and $\sigma$ ($p_{x\gamma}$) states which it is absent in the p-DOS of bulk.

The calculations reveal that compared to Zn K-edges in ZnO bulk and sheet, Zn K-edge in ZnS structures show a shift to lower energies. This is a result of larger bond lengths in ZnS structures, and that it can be used to fingerprint each structure. This is confirmed by the other ELNES spectra, discussed below.

3.2.2. Zn L$_{2,3}$ edge

A comparison between Fig. 7(d) and Fig. 8 (c$_{1,2}$) clarifies an intense similarity of Zn L$_{2,3}$-edge and partial DOS dispersions of ZnS bulk. As Fig. 8(c$_1$) confirms, the shoulder at the edge onset (at
2.40 eV) can be attributed to transition of 2p-electron to purely s-like states of Zn atom. In addition, like ZnO, the first strong peak in Zn L-edge can be assigned to a hybridization of p- and d-states. Except a shoulder at the edge onset, the other structures in Zn L-edge originate from the transition of 2p-electron to mostly d-like states of Zn atom. Whereas all the d-symmetries have some contributions in transitions, the contribution of t_{2g} (d_{xz}, d_{yz}) orbitals is more than the other symmetries. As Fig. 8(d_{1,2}) shows, like the bulk structure, the overall dispersion of unoccupied DOS of d-symmetry in ZnS nanosheet is similar to Zn L-edge. The first feature in Zn L-edge at 4.60 eV, which is a shoulder like structure, can be assigned to transition of 2p-electron to unoccupied states of s-d (e_{g}) hybridization. Compared to the bulk, the peak position of this shoulder in the nanosheet has a shift to higher energies equal to 0.3 eV. In addition, moving from bulk to nanosheet, some considerable differences, such as a shift to higher energies originated from the decrease in the bond length, are observable in the dispersions of Zn L-edge. Whereas in the onset of Zn L-edge of bulk, all the d-symmetry states have equal contributions, in the case of nanosheet, d_{2y^2-r^2} has the main role in transitions.

3.2.3. S K-edge

Fig. 9(e) and (f) shows the calculated S K-edge in the bulk and nanosheet of ZnS, respectively. As Fig. 9(d) confirms, the calculated S K-edge is an excellent agreement with the experimental XANES spectrum [53]. The main structures labeled by A1 to A4, B and C have been well reproduced. In the bulk, the contribution of σ state in transitions is nearly twice π states (Fig. 10(c)). Therefore, all the S K-edge structures in bulk can be assigned to transition to σ' orbitals. Compared to the bulk, the differences in S K-edge spectrum of ZnS nanosheet demonstrate that the bindings have changed. Compared to the bulk, except the first feature, all the ELNES structures in nanosheet have a shift to the lower energies. In addition, the shoulder-like ELNES structures A_3–A_4 have changed to be main peaks in nanosheet. There is an additional structure in S K-edge of nanosheet, occurred at 22.9 that it has no corresponding
in the bulk. As Fig. 10 (d) confirms, due to the same and large contributions of both $\pi (p_z)$ and $\sigma (p_{xy})$ states in the $p$-DOS, C structure can be attributed to transition to both $\pi'$ and $\sigma'$ states. Except the structure C and the first feature of S K-edge in nanosheet which in addition to $\sigma (p_{xy})$ state has a noticeable contribution of $\pi (p_z)$ state, the other features can be assigned to transition to mostly $\sigma$ state.

Finally, since the momentum dependency in the ELNES spectra of two-dimensional materials is important and it can provide noteworthy information on their anisotropic properties, we dealt with this dependency. Fig. 11 includes all the computational ELNES/XANES spectra with the momentum vector parallel ($q \parallel z$) or perpendicular ($q \parallel xy$) to the $c$-axis. It can be noted that although up to 25 eV beyond the Zn K ELNES/XANES onset in ZnO-NS the spectral features are mainly composed of $q \parallel xy$ component, the contribution of $q \parallel z$ component in first peak is considerable. Furthermore, the spectral features beyond the 25 eV are basically composed of

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**Fig. 9.** Left panels: (a) The experimental ELNES spectrum of O K-edge in ZnO bulk [45], and calculated O K-edge in (b) bulk and (c) sheet of ZnO. Right panels: (d) Experimental XANES spectrum of S K-edge in ZnS bulk [53], and calculated S K-edge in (e) bulk and (f) sheet of ZnS.

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**Fig. 10.** Left panels: unoccupied $p$-DOS of oxygen atom in (a) bulk and (b) sheet of ZnO. Right panels: unoccupied $p$-DOS of sulfur atom in (c) bulk and (d) sheet of ZnS.
Fig. 11. Zn K and L_{2,3}, and O and S K edges in ZnO and ZnS nanosheets for \( q \parallel xy \) (red thick lines) and \( q \parallel z \) (black thin lines) components. \( q \) is the scattering vector or momentum transfer of the incident electron. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

\( q \parallel z \) component. In ZnS-NS, except in the first peak, Zn K edge is composed of both \( q \parallel xy \) and \( q \parallel z \) components with the nearly equal contributions. Clear crystallographic dependence can also be predicted for the O and S K ELNES. Especially in the first pronounced peak of O K edge (peak B), the main contribution originates from the \( q \parallel xy \) component. Peak C is composed of both in-plane and out-of-plane components. In S K edge, the second peak is clearly composed of the in-plane (\( q \parallel xy \)) component, while overall dispersion of the other features is related to both \( q \parallel xy \) and \( q \parallel z \) elements. Compared to the case for K edge, the anisotropy of the spectra is small for the Zn L_{2,3} ELNES. This can be attributed to different atomic orbitals that are responsible for K and L_{2,3} edges. The first few eV of Zn K edge reflect mainly 4p-type orbitals, while the first few eV of the Zn L_{2,3} edge reflect mainly 4s orbitals. The spherical nature of the s orbital is the reason for the weaker dependence of the L_{2,3} edge on the orientation.

4. Conclusions

The energy loss near edge structures of ZnO and ZnS nanosheets was calculated in the framework of the density functional theory by means of the FPLAPW method and they were compared with those of ZnO and ZnS wurtzite crystal structures. Since the inclusion of core-holes was found to be essential for the accurate reproduction of features in ZnO and ZnS bulk edge structures, and due to the rather wide band gaps, it can be deduced that a full core-hole leads to the more reasonable ELNES spectra of Zn based nanosheets than a ground state. In addition to a full core-hole with converged sizes of super-cells, the magic angle conditions were required in order to reproduce all the edge structures. By means of local density of states and the ELNES decomposition to its \((I, m^*)\) components, the main structures were interpreted and the existing differences between the spectra of bulks and nanosheets were explained. Zn K-edges in bulks and sheets exhibit different properties. We could explain the differences between Zn K-edges in bulks and nanosheets by changing the bindings in formers and latters. The presence of sp^3 hybridization in nanosheets results in a \( \pi^* \) structure at the onset and a \( \sigma^* \) structure beyond the onset which this is the characteristic behavior of sp^2 hybridized materials. However, the main peaks in ZnO and ZnS bulks arise from transitions to mostly \( \sigma^* \) states. L_{2,3}-edge ELNES structures of Zn atom in ZnO and ZnS nanosheets were calculated and compared with those of wurtzite bulk structures. The main contributions in L_{2,3}-edge can be attributed to transition to mostly d-symmetry states and p-d hybridized orbitals. As a result of the smaller bond lengths in the nanosheet structures, all the ELNES spectra in nanosheets, including Zn K- and L_{2,3}-edges, and O and S K-edges show a shift to the higher energies. Moreover, the calculations reveal that compared to Zn edges in ZnO structures, all the ELNES spectra of ZnS structures including the bulk and sheet show a shift to lower energies. This is a result of larger bond lengths in ZnS structures, and that it can be used to fingerprint each structure. The orientation dependency of edge structures was also studied. Whereas the momentum dependency, and therefore, the anisotropy features of the spectra are small for the Zn L_{2,3} ELNES, they are important in the K-edge ELNES/XANES spectra of ZnX nanosheets. In addition, by means of the many-body G_0W_0 approximation, we showed that ZnS-NS is a wide band gap semiconductor with the energy gap equal to 5.83 eV.
References