Structural and elastic properties of WSe$_2$: first-principles calculations

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Abstract. By using the first principle density functional theory, we calculated the structural and elastic properties of WSe$_2$ crystals under different pressures. The results show that the compressibility of WSe$_2$ in the c-direction is much greater than that in the a-direction. The results of the elastic constants reveal that WSe$_2$ is mechanically stable under pressure 0 GPa to 50 GPa. The calculation results of elasticity-relevant properties show that the WSe$_2$ crystal is a brittle material and is solid with interatomic forces.

1. Introduction

After the initial boom in graphene research, layered transition metal dichalcogenides MX$_2$ (M = Ta, Nb, Ti, Mo, W, Cr, etc., X = Te, Se, S, etc.) have been a hot topic in recent years[1, 2]. Layered transition metal dichalcogenides MX$_2$ display various interesting physical properties. In chemical compound, the metal atom M is sandwiched between the two anion surfaces of X atom, and a strong covalent metal anion bond is formed between the metal atom M and the sulfur atom X. Along the c axis, there is a weak van der Waals force between sandwich layers [3, 4]. Because of these weak forces, sandwich layers can slide against each other, even providing smooth contact between metal atomic layers under stress.

As a member of these transition-metal dichalcogenides, the characteristics of WSe$_2$ under high pressure are inspiring people's interests. Vaidya et al [5] measure the electrical resistance on single crystals of WSe$_2$ under pressure from 0 GPa to 27 GPa. Experimental results show resistance decreases gradually under pressure for WSe$_2$. Bao Liu et al [6] measured the resistivity of WSe$_2$ in situ under high pressure. Their results indicate that the pressure can induce the phase transition of WSe$_2$ in isostuctural semiconductor-semimetal. Emre et al [7] conducted X-ray diffraction study of WSe$_2$ and did not discovered phase transition in the pressure range studied. By first principles calculation, Li et al [8] predicted that the semi metallic phase transition of WSe$_2$ semiconductor with equal structure occurs at 40 GPa.

In the present paper, we focus on investigation on structural and elastic properties of WSe$_2$ under higher pressure. Because WSe$_2$ usually works under pressure when it is used as a solid lubricant, the study of pressure behavior about this material is very useful.

2. Computational details and methods

In this work, the first-principles calculations were performed by using CASTEP program [9]. We applied the plane wave ultrasoft pseudopotential recommended by Vanderbilt [10] for the interaction of the electrons with the ion cores. The generalized gradient approximation (GGA) was adopted. Wu-Cohen (WC) exchange-correlation function was used. Pseudo-atom calculations are carried out...
for W-5s²5p⁶5d⁶6s² and Se-4s²4p⁴. Using plane-wave basis set extended the electronic wave functions. Energy cut-off of electronics employed 450 eV. For the Brillouin sampling, we used the 5 × 5 × 2 Monkhorst–Pack meshes. For ensuring self-consistent convergence, the convergence criteria of the total energy is set to within 5.0 × 10⁻⁶ eV/atom. The convergence criteria of maximum force is 0.01 eV/Å. The convergence criteria adopted 0.02 GPa for maximum stress and 5.0 × 10⁻³ Å for maximum displacement. For calculating elastic properties, the difference of convergence of energy was set to 1×10⁻⁶ eV/atom. The difference of convergence was 0.002 eV/Å for the maximum force. The difference of convergence was 1×10⁻⁴ for the maximum displacement and 0.003 GPa for the maximum strain amplitude.

3. Results and discussion

WSe₂ crystal is a hexagonal layered crystal structure with the space group $P6_3/mmc$ ($D_{6h}^4$) (No. 194) [11]. To obtain the ground state structure of WSe₂, we get a series of $E_m$-$V$ (as shown in Fig. 1) data of WSe₂. The $E_m$-$V$ data is fitted to the third-order Birch–Murnaghan equation of state (EOS) [12]. The results of structural parameters $a_0$, $c_0$, $c_0/a_0$ and $V_0$ of WSe₂ are acquired at 0 K and 0 GPa and are listed in Table 1. Other theoretical [8, 13] and experimental values [11, 12, 14] are also listed in Table 1. We compared our calculated values with the experimental values [12]. The relative errors of cell parameters $a_0$ and $c_0$ are 0.16% and 0.52% respectively. The relative error of the parameter $c_0/a_0$ and the volume $V_0$ are 0.35% and 0.85% respectively. The relaxed cell parameters are also listed in Table 1. The relative errors of relaxed results are 0.37%, 0.85% and 0.47%, respectively for cell parameters $a_0$, $c_0$ and $c_0/a_0$. Compared with other experimental data, the relative error of our calculation results is also within 1%. It can be deduced that the computational methods used in this work is suitable and the results are reliable.

![FIG. 1. Energy as a function of the primitive cell volume of WSe₂.](image)

| Lattice parameters | $a_0$ (Å) | $c_0$ (Å) | $c_0/a_0$ | $V_0$ (Å³) |
|--------------------|----------|----------|-----------|------------|
| This work (EOS)    | 3.287    | 13.028   | 3.963     | 121.9261   |
| This work (relaxed)| 3.294    | 13.070   | 3.968     | 122.8295   |
| Cal.(GGA+PW91) [8] | 3.299    | 13.092   | 3.969     | 123.396    |
| Cal.(LDA) [13]     | 3.285    | 12.748   | 3.881     | 119.136    |
| Exp.[9]            | 3.279    | 12.963   | 3.954     | 120.670    |
| Exp. [11]          | 3.282    | 12.960   | 3.949     | 120.900    |
| Exp. [14]          | 3.290    | 12.970   | 3.942     | 121.580    |
In Fig. 2, we plot the curves of our calculated and the experimental [7] cell parameters $a/a_0$, $c/c_0$ and $V/V_0$ with increasing pressure from 0 GPa to 50 GPa. In Fig. 2, the $a_0$, $c_0$ and $V_0$ are the ground state parameters. Our results are well consistent with the experimental data. The value of $a/a_0$ is bigger than that of $c/c_0$ at the same pressure, indicating that the lattice constant $a$ is not sensitive to pressure relative to the lattice constant $c$. At the beginning, the $c/c_0$ decreases steeply with the increasing pressure and then it becomes gentle. The $a/a_0$ almost decreases linearly with increases of pressure. At 35 GPa, the $c$-axis decreases by 12.18% and $a$-axis reduces to 7.24%. It distinctly implies that the $a$-direction of the hexagonal WSe$_2$ is much more uncompressible than the $c$-direction. Fig. 3 illustrates the change of the axial reductions ratio $((c/c_0)/(a/a_0))$ with pressure. Our calculated results are in good agreement with the experimental data [7]. The axial reduction ratio decreases sharply with increasing pressure at low pressures (< 20 GPa), and then decreases slowly as increase of pressure. It indicates that, at low pressures, the relatively very weak Van der Waals forces between adjacent Se–Se planes leads to the high compression rate. At higher pressures, the repulsive force rapidly increases between Se atoms in adjacent layers because of the Se atoms closing to each other. The repulsive force between Se atoms becomes comparable with the W–Se intra-bond. So the $c$-axis reduction rate of WSe$_2$ is lowered.

![FIG. 2. The pressure dependences of $a/a_0$, $c/c_0$, $V/V_0$ of WSe$_2$.](image)

![FIG. 3. The ratio of the axial reductions of WSe$_2$ as a function of pressures.](image)

Elastic properties of materials contribute to understand the mechanical stability and the Debye temperature of materials. Hence, it is useful to study elastic properties of WSe$_2$. Usually, there are 21 non-zero independent elements for elastic stiffness tensor. However, it can be further reduced because of the higher symmetry of the crystal. For WSe$_2$, there are five independent components in its elastic tensor, i.e. $C_{11}$, $C_{33}$, $C_{44}$, $C_{12}$ and $C_{13}$. The calculated elastic constants of WSe$_2$ are listed in Table 2.
together with previously experimental [15] and theoretical values [8, 16] at ground state. It can be seen that our result is well consistent with theoretical results and obtained experimental data. In ground state, $C_{11} = C_{22} = 203.19$ GPa is much bigger than $C_{33} = 68.31$ GPa, indicating $c$-axis is very easier to shrink and will have a larger strain under the normal stress with the same value. This difference among the elastic constants also shows WSe$_2$ is mechanically anisotropic. Table 2 also lists the obtained elastic constants of WSe$_2$ under pressure up to 50 GPa. We can see that $C_{11} = C_{22}$ is smaller than $C_{33}$ at pressure $p\geq 20$ GPa except of that at 40 GPa, which indicates that, with pressure increasing, $c$-axis become harder to shrink under the normal stress with the same value. For hexagonal crystals, the criteria of the mechanical stability under isotropic pressure is $C_{44} > 0$, $C_{11} > |C_{12}|$, $C_{33}(C_{11}+C_{12})>2C_{13}^2$, where $C_{aa} = C_{aa} - P (a=1, 2, 3)$, $C_{12}=C_{12} + P$ [17]. From table 2, we can see that all the elastic constants satisfy these conditions, which indicates WSe$_2$ is mechanically stable in the pressure range from 0 to 50 GPa.

Table 2. Elastic constants $C_{ij}$ (GPa), bulk modulus $B$ (GPa) of WSe$_2$ under different hydrostatic pressures, together with the other experimental and theoretical data.

| Pressure | $C_{11}$  | $C_{33}$  | $C_{44}$  | $C_{12}$  | $C_{13}$  | $B$  |
|----------|-----------|-----------|-----------|-----------|-----------|------|
| 0        | 203.19    | 68.30     | 31.39     | 39.48     | 19.89     | 61.51|
| Pref. [8]| 190.76    | 59.62     | 39.26     | 41.71     | 21.18     | 63.7 |
| Pref. [15]| 200     | 50        |           |           |           | 72.7 |
| Pref. [16]| 147     |           | 40        |           |           |      |
| 10       | 340.31    | 236.28    | 85.74     | 74.58     | 73.27     | 148.94|
| 20       | 347.94    | 354.32    | 142.82    | 86.60     | 102.90    | 181.59|
| 30       | 396.80    | 400.98    | 145.17    | 103.05    | 118.96    | 208.45|
| 40       | 471.39    | 353.83    | 192.34    | 128.56    | 92.41     | 210.91|
| 50       | 517.01    | 600.67    | 200.33    | 150.75    | 189.95    | 298.04|

Based on the elastic constants, we get the bulk modulus $B$, shear modulus $G$, $B/G$ value for WSe$_2$ under pressure 0 GPa to 50 GPa, as shown in table 3. The value of the bulk modulus at ground state is about 61.51 GPa and are well consistent with the experimental results (72.2 GPa)[18] and other theoretical results 63.7 GPa [19]. From table 3 we can see that the bulk modulus $B$ is bigger than the shear modulus $G$ at a given pressure. It discloses that the shear deformation is easier to occur and the shear modulus is the parameter limiting the stability of WSe$_2$. Brittle or ductile have a significant effect on the application of a material. To distinguish them, Pugh [20] proposed that the material behaves in a brittle manner if $B/G < 1.75$, otherwise, the material is ductile. Our calculated result shows that the value of $B/G$ is smaller than 1.75 under the pressures from 0 GPa to 50 GPa, indicating that WSe$_2$ is brittle in this pressure range.

Young’s modulus ($E$) can reflect the stiffness of solids. The larger the value of $E$ is, the stiffer the material is. At 0 GPa, the $E$ value of WSe$_2$ is 116.92 GPa. With the increase of applied pressure, the value of $E$ increases, indicating that the pressure can enhance the stiffness of WSe$_2$ crystal. The characteristic of the bonding forces can be provided by Poisson’s ratio of the material. For central force solids, the lower limit and upper limit of Poisson’s ratio are 0.25 and 0.5 respectively [21]. Poisson’s ratio of WSe$_2$ is smaller than 0.25 from 0 GPa to 50 GPa, suggesting that the interatomic forces within WSe$_2$ crystal is noncentral under this pressures. On the other hand, Poisson’s ratio reflects the stability of a crystal against shear. It is the ratio of transverse contraction strain versus longitudinal extension strain under a stretching force. With increasing pressure, the variation of Poisson’s ratio of WSe$_2$ is very slight, indicating that WSe$_2$ is stable against shear with pressure.

Table 3. Bulk modulus $B$ (GPa), shear modulus $G$ (GPa), $B/G$ values, Young’s modulus $E$ (GPa), Poisson’s ratio $\sigma$ under different hydrostatic pressures $P$ (GPa).

| $P$ | $B$ | $G$ | $B/G$ | $E$ | $\sigma$ |
|-----|-----|-----|-------|-----|---------|
| 0   | 61.52 | 49.41 | 1.24  | 116.92 | 0.18    |
4. Conclusions

We have studied the structure and elastic related mechanical properties of WSe$_2$ under pressure by using the density functional theory of the first principle. The acquired cell parameters and elastic constants results of WSe$_2$ all show that $c$-axis is very easier to be compressed at low pressures, but $c$-axis become harder to be compressed under higher pressures (>20 GPa). Calculated elasticity-relevant shear modulus and bulk modulus indicate WSe$_2$ crystals are brittle in this pressure range 0 GPa to 50GPa. Young’s modulus reflects that the pressure can strengthen the stiffness of WSe$_2$. The results of Poisson’s ratios reveal that the interatomic forces within WSe$_2$ are noncentral under the pressures from 0 GPa to 50 GPa.

Acknowledgments

This work was supported by the China National Natural Science Foundation (Grants No. 11847163).

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