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THEORETICAL STUDY OF THE STRUCTURAL, ELASTIC AND EQUATION OF STATE OF CHALCOPYRITE STRUCTURE $AgAlS_2$

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The ground state parameters such as lattice constants, bulk modulus and elastic constants are calculated for chalcopyrite structure $AgAlS_2$ by using density functional theory (DFT). The obtained lattice constants and elastic constants are agree well with available theoretical or experimental results. The bulk modulus B, shear modulus G, Young's modulus E and wave velocity of $AgAlS_2$ are also obtained for the first time. In addition, the equation of state of $AgAlS_2$ in the pressure range of 0-10 GPa and up to a temperature of 1000 K has also been obtained.

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1. Introduction

Very recently, ternary chalcopyrite semiconducting compounds with the general formula I-III-VI_2, e.g. (I =Cu, Ag; III =Al, Ga, In; VI = S, Se, or Te), have been gaining a considerable attention due to their uses in photocathodes for water splitting or nonlinear optical (NLO)[1-6]. Some compounds of I-III-VI_2 family like $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$, have excellent NLO properties and are suitable for applications of NLO devices. $AgAlS_2$, $AgAlSe_2$, $AgAlTe_2$ were studied as the promising photocathodes for water splitting and photovoltaic detectors. Although the structure, elastic and optical of the above compounds are accessible from first-principles calculations [7-9]. Compared to the $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$, the $AgAlS_2$ crystal has not been investigated adequately. There are some theoretical researches have been done on $AgAlS_2$, however, most of them are focused on structural, electronic and optical properties [**9**]. Few pay attention to elastic constants and equation of state under high temperature and pressure, which are important to extend our knowledge to $AgAlS_2$ performance. Therefore, it is necessary to study temperature and pressure influences on equation of state of $AgAlS_2$. The $AgAlS_2$ crystal experimentally found to crystallize in chalcopyrite structure phase with space group No.122 (I42d), as shown in Fig. 1.

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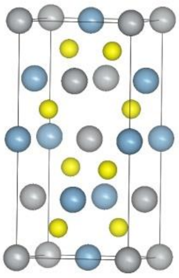

Fig. 1. The crystal structure of $AgAlS_2$. (The Ag atoms are shown as gray spheres, Al as blue spheres and the S atoms as yellow spheres)

The present work aims to study the structural and elastic properties and obtain the equation of state of $AgAlS_2$ crystal under different pressures using the density functional theory and the quasi-harmonic Debye model [10].

2. Computational methods

In the present work, all the calculations are performed using the CASTEP code, based on the density functional theory[11]. The Vanderbilt ultrasoft pseudopotential [12] is used with the cutoff energy of 570 eV for the considered structure. The *k* point meshes of 8×8×7 for chalcopyrite structure $AgAlS_2$ is generated using the Monkhorst-Pack scheme[13]. The electronic exchange-correlation potentials are described within within the generalized gradient approximation (GGA) proposed by Perdew et al.[14] and the local density approximation (LDA) parameterized by Perdew-Zunger (CA-PZ) [15].

3. Results and discussion

3.1. Structural properties

In Table 1, we listed our results together with the available experimental data and other theoretical results. The errors of lattice parameters (a, c) for the $AgAlS_2$ from LDA and GGA, calculations are (-2.94%, 1.64%) and (+0.6%, +2.46%), respectively. All these results show that the results obtained from GGA calculation are in better agreement with the experimental data [16] than those from LDA method. As is seen from Table 1, It shows that the bulk modulus B calculated by GGA is lower than other theoretical with the error of -14.6%. However, the bulk modulus B calculated by LDA deviates by 10.45% with respect to other theoretical results.

Table 1 Calculated lattice parameters a and c (Å), bulk modulus B (GPa) and its first pressure derivativ B' for calculated $AgAlS_2$, compared to available experimental and theoretical values

	This work			Other theoretical calculations		Experiments
a	5.5273[a]	5.7293[b]	5.7369[c]	5.647[d]	5.48[e]	5.695[f]
c	10.4281[a]	10.5122[b]	10.5262[c]	10.057[d]	10.44[e]	10.26[f]
B	84.22[a]	65.11[b]	67.95[c]	76.25[d]		
B'			4.58[c]	5.1[d]		

[a] LDA,[b]GGA,[c]Fit,[d]Ref.[9], [e]Ref.[17],[f]Ref.[16]

3.2 Elastic properties

The number of independent elastic constants is different for various crystal structures. For a tetragonal chalcopyrite crystal, they are six independent elastic constants (C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}). The mechanical stability criteria are given by Born stability criteria [18].

As shown in Table 2, our calculated values of elastic constants bey the mechanical stability criteria for chalcopyrite crystal, indicating that the $AgAlS_2$ is mechanically stable. Unfortunately, there are no experimental results for comparison with our elastic results for $AgAlS_2$. The calculated elastic constants in this work are in agreement with the previous results [8].

Table 2 Calculated elastic constants C_{ij} (in GPa) of $AgAlS_2$

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
LDA	108.5	73.62	73.38	100.96	40.31	40.12
GGA	87.55	53.44	55.50	80.18	37.34	35.65
Ref[8]	95.6	70.8	70.3	94.8	23.4	14.9

Based on the known C_{ij} values, it is easy to study the linear compressibilities χ_a and χ_c along the *a* and *c* axes and the volume compressibility χ [19] that are listed in Table 3:

$$\chi_a = -\frac{1}{a}\frac{\partial a}{\partial p}\Big|_{p=0} = \frac{c_{33}-c_{13}}{c_{33}(c_{11}+c_{12})-2c_{13}^2} \tag{1}$$

$$\chi_c = -\frac{1}{c}\frac{\partial c}{\partial p}\Big|_{p=0} = \frac{c_{11}+c_{12}-2c_{13}}{c_{33}(c_{11}+c_{12})-2c_{13}^2} \tag{2}$$

$$\chi = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{p=0} = 2\chi_a + \chi_c \tag{3}$$

Table 3. Calculated elastic compliances S_{ij} (in TPa^{-1}) as well as linear and volume compressibilities χ_a, χ_c, χ (in TPa^{-1}) of $AgAlS_2$

	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	S_{66}	χ_a	χ_c	χ
LDA	20.79	-7.60	-9.59	23.84	24.81	24.93	3.62	4.56	11.8
GGA	22.45	-6.87	-10.79	27.40	26.78	28.05	4.80	5.83	15.43

The obvious discrepancy of χ_a and χ_c of $AgAlS_2$ crystal demonstrates that the effect of hydrostatic pressure along *c* axis is approximately 1.26 times greater than that along *a* axis.

In order to study $AgAlS_2$ elastic nature systematically, we further investigated the other interesting elastic quantities for $AgAlS_2$ such as the bulk modulus *B*, shear modulus *G*, and the Young's modulus *E*. The polycrystalline elastic properties, including bulk modulus *B*, shear modulus G, Young's modulus E, can be obtained by Voigt-Reuss-Hill (VRH) approximation [20-22]. The B, G and E are listed in Table 4.

Table 4. Calculated bulk modulus B (GPa), shear modulus G (GPa),Young Modulus E (GPa), the compressional wave V_p (Km/s), the shear velocities V_S (Km/s), average wave velocity V_m (Km/s) and Debye temperature (θ) of $AgAlS_2$

	B	G	E	V_p	V_S	V_m	θ
LDA	84.30	28.01	75.65	5.25	2.52	2.83	317.44
GGA	64.87	25.64	67.97	5.08	2.59	2.90	325.28

In addition, Debye temperature and sound velocity are also essential physical quantities to distinguish many physical properties [23]. The values of the compressional velocity wave V_p and the shear wave velocity V_S can be determined using the Navier's equation [24], where ρ is density of material.

$$V_p = \sqrt{(B + \frac{4}{3}G)\frac{1}{\rho}} \tag{4}$$

$$V_S = \sqrt{\frac{G}{\rho}} \tag{5}$$

and the average wave velocity V_m can be calculated by

$$V_m = [\frac{1}{3}(\frac{2}{V_s^3} + \frac{1}{V_p^3})]^{-1/} \tag{6}$$

Debye temperature θ calculated from elastic constants is the same as that determined from specific measurements at low temperature. Debye temperature θ can be calculated from the famous average sound velocity V_m, by the following relation given in [25]

$$\theta = \frac{h}{k}[\frac{3n}{4\pi}(\frac{N_A \rho}{M})]^{1/3} \upsilon_m \tag{7}$$

h is Planck's constant, k is Boltzmann's constant, N_A is Avogadro's number, n is the number of atoms per formula unit. M is the molecular weight, ρ is the density of material.

The calculated sound velocity of V_p, V_S, V_m and θ for the $AgAlS_2$ compounds are listed in Table 4. Unfortunately, no experimental or theoretical works exist on sound velocities of $AgAlS_2$ for comparison with our results. We expect that our theoretical results provide the valuable reference for the further research. In this work, the calculated Debye temperature $\theta =$ 317.44 K. The value is in reasonable agreement with the value 314.6 K computed in terms of the simple relations [26]. This suggests that the Debye temperature θ calculated from elastic constants is correct.

A thorough investigation of the elastic anisotropic behavior of a solid material, the three dimensional (3D) surface constructions of the directional dependences of reciprocals of Young's modulus E are very useful. The expressions of the reciprocals of Young's modulus are different due to their various crystal structures [27]. For tetragonal crystals, it is defined as follows

$$\frac{1}{E} = S_{11}(l_1^4 + l_2^4) + (2S_{13} + S_{44})(l_1^2 l_3^2 + l_2^2 l_3^2) + S_{33} l_3^4 + (2S_{12} + \tag{8}$$

where l_1, l_2 and l_3 represent the directional cosines with respect to the x, y and z axes. Using the calculated compliance constant S_{ij}, which is the inverse of the elastic tensor C_{ij}, we obtained the directional Young's modulus for $AgAlS_2$ as shown in Fig.2.

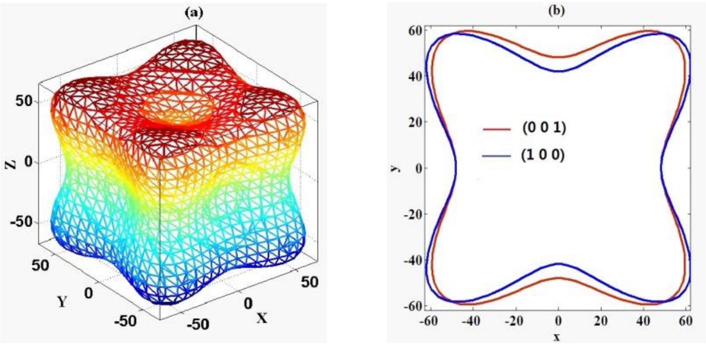

Fig. 2. Direction-dependent Young's modulus (GPa) of $AgAlS_2$. The (001) plane refers to the plane that intersects the image horizontally at $E_z = 0$; the (100) plane refers to the plane that intersects the image vertically at $E_x = 0$; the [001] direction along the Ez

For $AgAlS_2$, at ground state the obtained Fig.2a deviates a little from the spherical shape, which means that $AgAlS_2$ has a highly elastic anisotropy, and the isotropy in the (001) plane is worse than that of the (100) plane, as shown in Fig.2b.

3.3 Equation of state

The equation of state is used to describe the thermodynamic properties of materials under pressure and temperature [10]. We calculated the equation of state of $AgAlS_2$ in the pressure range of 0-10 GPa and up to a temperature of 1000 K.

In order to obtain the stable structure of $AgAlS_2$ with chalcopyrite symmetry, the total energy as a function of the unit-cell volume at the equilibrium cell volume V_0 has been calculated, as shown in Fig.3. The lattice constants (*a* and *c*), bulk modulus B and its pressure derivative B' (Table 1) have also been estimated by fitting Birch-Murnaghan's equation of state [28]. It is seen that our calculations agree very well with the experimental and theoretical results.

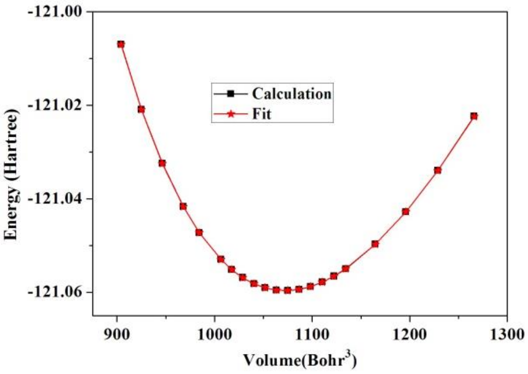

Fig. 3. Total energies as the function of the unit cell volumes for $AgAlS_2$.

Fig. 4 and Fig. 5 shows the V/V_0-T and V/V_0-P. The V/V_0-T equations of state for P = 2, 4, 6, 8 and 10 GPa are shown in Fig. 4a, as pressure increases, the curve of V/V_0-T becomes softened. The V/V_0 - P equations of state for T = 0, 300, 600 and 900 K are plotted in Fig. 4b. As can be seen, as temperature increases, the curve of V/V_0-P becomes steeper, indicating that $AgAlS_2$ is compressed much more easily with increasing temperature.

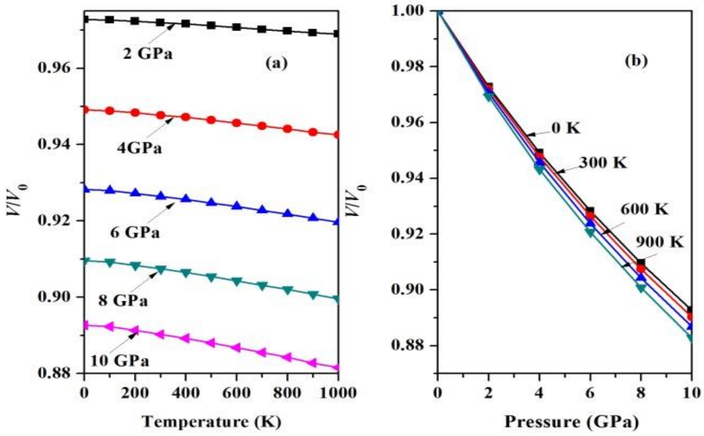

Fig. 4. V/V_0 of the $AgAlS_2$ at various pressures and temperatures

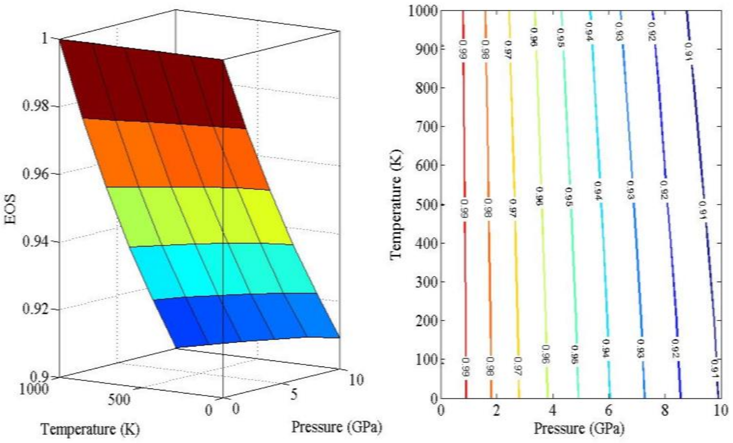

Fig. 5. V/V_0 versus temperature and pressure for $AgAlS_2$ (a) three-dimensional plot (b) contours

4. Conclusions

In conclusions, the GGA and LDA potentials are applied to obtain the structural, elastic of chalcopyrite structure $AgAlS_2$. The lattice constants, bulk modulus and elastic constants are also obtained, which are consistent with the available theoretical results. The elastic constants, bulk modulus, shear modulus, Young's modulus and wave velocity of $AgAlS_2$ are successfully obtained. The direction dependence of Young's modulus shows that $AgAlS_2$ is an elastically anisotropic. Moreover, through the quasi-harmonic Debye model, the equation of state for $AgAlS_2$ under pressure and temperature was also systematically obtained.

Acknowledgments

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