Ab-initio Investigation of Elastic Properties of Monoclinic $ZnAs_2$ Crystal

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Abstract

Elastic properties of monoclinic $ZnAs_2$ crystal are studied under the PBEsol scheme using the CRYSTAL Program. Independent elastic stiffness coefficients have been computed. Various elastic properties, such as shear modulus, bulk modulus, Young's modulus and Poisson's ratio have been analyzed. The directional dependence of the computed Young's modulus and linear compressibility is studied using ELATE software. Our investigation reveals the finite elastic anisotropy of the monoclinic $ZnAs_2$ crystal.

Keywords: $ZnAs_2$, *Ab-initio*, Elastic properties, Elastic anisotropy.

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Introduction

Monoclinic $ZnAs_2$ is a semiconducting compound of the II-V group [1]. $ZnAs_2$ has a monoclinic crystal structure with space group $P2_1/c$ (C_{2h}^5) [2-3]. Its unit cell has eight formula units [2]. The energy band gap is nearly 1eV [4-5]. There is tetrahedral coordination of atoms with a slight distortion of the tetrahedral structure [6]. $ZnAs_2$ crystals are useful for optoelectronic applications, such as light modulators, optical filters, lenses, etc. [7]. Anisotropy in the thermoelectric power of these crystals is useful for nonselective radiation detectors [8]. Soshnikov *et al* studied the elastic properties of $ZnAs_2$ crystals with ultrasound measurements [9]. These crystals may be utilized for the fabrication of polarization-controlled switches due to their polarization photosensitivity [10]. Photosensitive Schottky barriers may be formed on monoclinic $ZnAs_2$ crystals [10]. The variation of index of refraction of $ZnAs_2$ crystal may be utilized in fabricating infrared polarizers [11-12]. Our interpretation of the elastic properties of $ZnAs_2$ may have considerable practical utility in device design for future research. For optimum performance of the device, knowledge of the direction-dependent elastic anisotropy of $ZnAs_2$ crystals provides advantages in determining the preferred orientation of the crystals.

Computational details

Ab-initio investigation of monoclinic $ZnAs_2$ is performed with CRYSTAL Code [13-14]. In the present study, the DFT exchange-correlation functional GGA is employed. The basis sets for Zn and As atoms have been utilized from the CRYSTAL-Basis Set Library [13-14]. Using initial geometry [3], optimization is performed and optimized lattice parameters and fractional coordinates are obtained. In this computation, the PBEsol [15] technique is implemented. The SCF convergence TOLDEE is set to 8. The calculations are performed using an 8 × 8 × 8 Monkhorst-Pack **k**-point mesh [16]. This **k**-point mesh corresponds to 125 **k**-points in the irreducible Brillouin zone. The BROYDEN parameter [13-14, 17-18] is also implemented to obtain convergence. The elastic properties [19-20] are studied at the equilibrium volume with a strain step of 0.01. The ELASTCON keyword is used for the computation of the elastic properties of monoclinic $ZnAs_2$ crystals. ELATE software [21-22] is used for the analysis of elastic quantities.

Results and Discussion

Elastic Properties

The analysis of elastic anisotropy is useful for understanding the direction-dependent elastic stretchability of crystals. This analysis is useful for engineering device design. The monoclinic crystal system has thirteen

independent elastic stiffness constants [23]. Using the initial geometry [3] with lattice parameters a = 9.287 Å, b = 7.691 Å, c = 8.010 Å, optimized lattice parameters have been obtained by CRYSTAL Code [13-14]. Using the optimized lattice parameters and fractional coordinates, the elastic stiffness constants of the monoclinic $ZnAs_2$ crystal are obtained, which are shown in table 1.

Table 1: Elastic stiffness constants (in GPa) of $ZnAs_2$ at zero pressure.

	Scheme	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
Present Work	PBEsol	126.72	63.47	59.95	– 4.41	136.81	38.35	6.07	145.84	1.75	26.73	4.23	44.58	44.18
Other Work[a]		95.63	31.47			102.5			112.6		20.76			40.45

[a] *Ref. [9, 24].*

Table 2. Computed values[b] of shear modulus G (in GPa), bulk modulus B (in GPa), Young's modulus E (in GPa) and Poisson's ratio ν (unitless) of $ZnAs_2$.

	B_V	B_R	B_H	G_V	G_R	G_H	E_V	E_R	E_H	ν_V	ν_R	ν_H
Present Work[b]	81.44	81.28	81.36	39.60	36.67	38.14	102.24	95.63	98.95	0.291	0.304	0.297

[b] *Values of B, G, E and ν have been computed with the help of ELATE software [21, 22]*

Table 3. Variations[c] of Young's modulus E (in GPa), shear modulus G (in GPa), Poisson's ratio ν (unitless) and linear compressibility β [in $(\mathrm{TPa})^{-1}$] of $ZnAs_2$.

	G_{min}	G_{max}	E_{min}	E_{max}	β_{min}	β_{max}	ν_{min}	ν_{max}
Present Work	25.76	51.76	70.92	121.47	3.60	4.45	0.051	0.491

[c] *These values of G, E, β and ν have been computed through ELATE software.*

Table 1 shows that the elastic constant C_{33} is greater than other elastic constants. It is obvious from table 1 that the value of C_{22} is greater than C_{11} at zero pressure. Elastic stiffness constants C_{44} and C_{66} are significantly smaller than the other elastic stiffness constant C_{11}.

Voigt bulk modulus (B_V) and Reuss bulk modulus (B_R) may be represented as a function of elastic stiffness constants C_{ij} and elastic compliance constants S_{ij} [25, 26]

$$B_V = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}] \quad (1)$$

$$B_R = [S_{11} + S_{22} + S_{33} + 2S_{12} + 2S_{13} + 2S_{23}]^{-1} \quad (2)$$

Reuss shear modulus (G_R) and Voigt shear modulus (G_V) are represented by [25, 26]

$$G_R = 15[4(S_{11} + S_{22} + S_{33}) + 3(S_{44} + S_{55} + S_{66}) - 4(S_{12} + S_{13} + S_{23})]^{-1} \quad (3)$$

$$G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}] + \frac{1}{5}[C_{44} + C_{55} + C_{66}] \quad (4)$$

The Voigt-Reuss-Hill approximation provides the estimated polycrystalline shear (G_H) and bulk moduli (B_H) [25-27]

$$G_H = \frac{1}{2}[G_R + G_V] \quad (5)$$

$$B_H = \frac{1}{2}[B_R + B_V] \quad (6)$$

Also, macroscopic polycrystalline Poisson's ratio ν_H and Young's modulus E_H may be represented as follows [25-27]:

$$E_H = \frac{9B_H G_H}{3B_H + G_H} \quad (7)$$

$$\nu_H = \frac{3B_H - 2G_H}{2(3B_H + G_H)} \quad (8)$$

The computed elastic moduli from elastic constants are shown in table 2.

The malleable property of a polycrystalline substance is expected to have a ratio of bulk modulus to shear modulus greater than about 1.75 [28]. The obtained value of Young's modulus shows sufficient stiffness of $ZnAs_2$. The value of

81.36 GPa of bulk modulus shows the ample material strength of $ZnAs_2$ crystals under deformation. The computed value of 0.297 of Poisson's ratio is within the theoretical limits [29] for materials. Maximum and minimum values of Young's modulus, shear modulus, Poisson's ratio and linear compressibility of $ZnAs_2$ are shown in table 3.

The elastic anisotropy of a crystal may be expressed as [30, 31]

$$A_B = \frac{B_V - B_R}{B_V + B_R} \quad (9)$$

$$A_G = \frac{G_V - G_R}{G_V + G_R} \quad (10)$$

The calculated values of anisotropy parameters A_B and A_G are 0.00098 and 0.0384 respectively.

Ranganathan *et al* [32] expressed the universal elastic anisotropy index in the following manner:

$$A^U = \frac{B_V}{B_R} + 5\frac{G_V}{G_R} - 6 \quad (11)$$

The obtained value of Ranganathan's universal elastic anisotropy index for $ZnAs_2$ is 0.402. All these finite values of anisotropy parameters indicate the presence of finite anisotropy in $ZnAs_2$ crystals. For isotropic materials, the value of each of the anisotropy parameters A_B, A_G and A^U is zero. With the help of ELATE software [21-22], the directional dependence of Young's modulus E and linear compressibility β is plotted in figures 1, 2 and 3. It is evident from figures 1 and 2 that directional Young's modulus has anisotropy. Similarly, figures 3 and 4 show the sufficient anisotropy of linear compressibility in $ZnAs_2$ crystal.

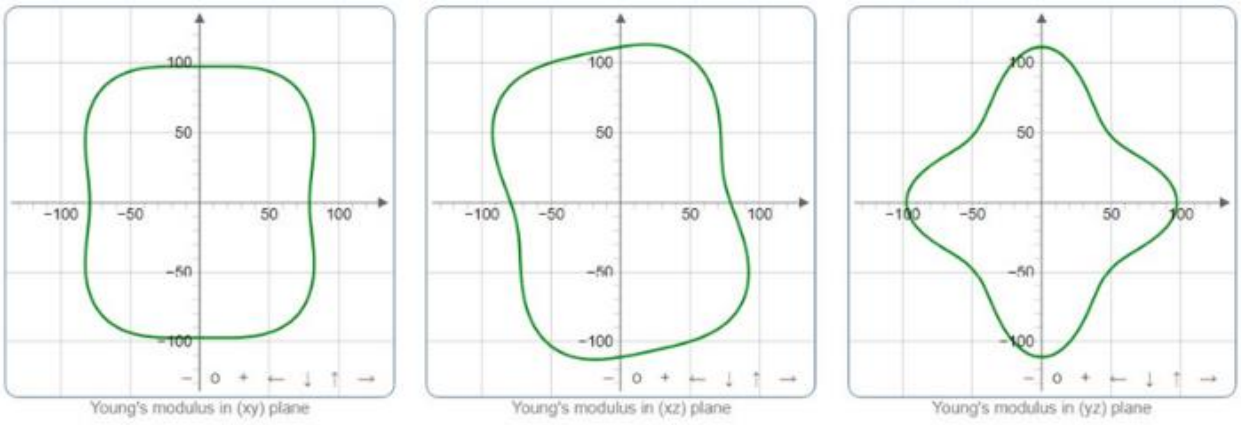

Figure 1. Directional dependence of the Young's modulus E (in GPa) of $ZnAs_2$

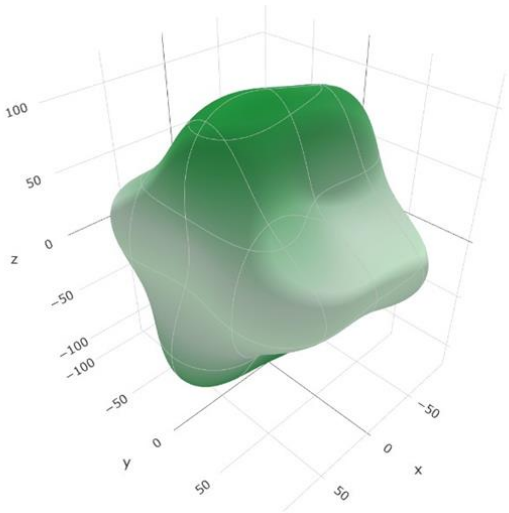

Figure 2. 3D View of the directional Young's modulus E (in GPa) of $ZnAs_2$

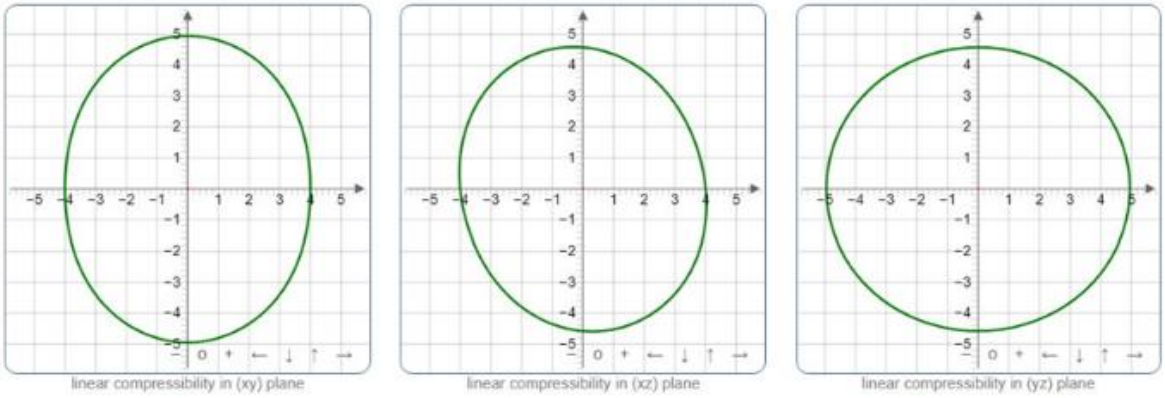

Figure 3. Directional dependence of the computed linear compressibility β [in $(\mathrm{TPa})^{-1}$] of $ZnAs_2$

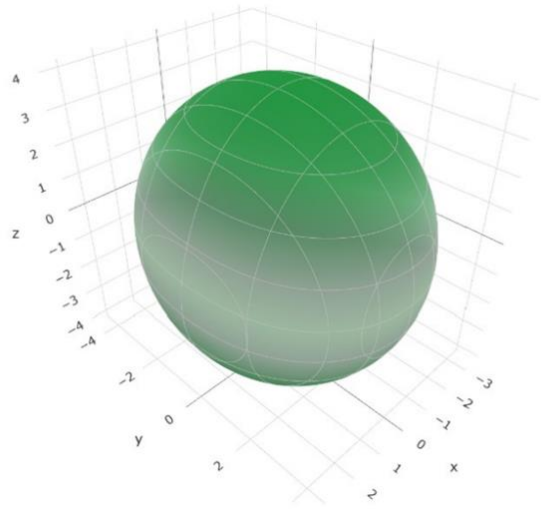

Figure 4. 3D View of the directional linear compressibility β [in $(\mathrm{TPa})^{-1}$] of $ZnAs_2$

Conclusion

The investigation reveals the various elastic properties of $ZnAs_2$ by using the GGA-PBEsol functional in the CRYSTAL program. Our investigation predicts the malleable nature of $ZnAs_2$. In the present findings, the obtained value of Ranganathan's universal elastic anisotropy index for $ZnAs_2$ is 0.402. It can be concluded from the study that $ZnAs_2$ has definite elastic anisotropy. Our present findings show that variation in the value of Young's modulus from its minimum value to its maximum value is 50.55 GPa. For the shear modulus, the variation in the value from minimum to maximum is 26 GPa. Our investigation of the anisotropic properties of $ZnAs_2$ may shed light on the preferred orientation of crystals for designing engineering devices using $ZnAs_2$ crystals.

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