Ab Initio Study on Electronic and Elastic Properties of $AgCr_2S_4$

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The structural, magnetic, electronic, and elasticity properties of a novel ternary silver-based chromium sulfo-spinel system ($AgCr_2S_4$) were investigated using first principles calculations as implemented in the Vienna Ab Initio Simulation Package with the generalized gradient approximation and meta-generalized gradient approximation. The spin effects on the $AgCr_2S_4$ compound have been studied relying on the energy–volume curves obtained for different magnetic phases (antiferromagnetic, ferromagnetic, and paramagnetic). It is indicated that this spinel material has a ferromagnetic nature. The electronic band structure and partial density of state results are presented in detail. The observed band gaps in majority and minority spin channels in the electronic band structure as $E_g = 0.75$ eV and $E_g = 0.57$ eV for generalized gradient approximation and as $E_g = 1.46$ eV and $E_g = 1.19$ eV for meta-generalized gradient approximation imply that the studied system has a semiconductor character. The polycrystalline elastic moduli are estimated based on the single-crystal elastic constants, and the mechanical stabilities are verified. In the aspect of the examined mechanical properties, the system is also a ductile material. This sulfo-spinel system can be a promising candidate for spintronics applications with a semiconducting electronic behavior as well as its mechanical durability.

topics: semiconductor, *ab initio*, elasticity, sulfo-spinel

1. Introduction

For decades, magnetic materials have been attracting great attention of materials scientists due to their wide usage in various technological areas such as spin-based electronic devices, biomedical applications, data-storage media, magneto- and electro-optics, and magnetic refrigeration [1–5]. In this context, especially the ternary chromium chalco-spinels ACr_2Ch_4 (Ch = S, Se and Te), which have fascinating magnetic and electronic properties such as magnetocapacitance [6, 7], magnetic resistivity [8] and semiconducting nature [9, 10], have been investigated both experimentally and theoretically [11–21]. This type of chalcogenides (ACr_2Ch_4) in which A element is usually taken from transition metals [11–13] is crystallized in a face-centered cubic structure including 14 atoms in the primitive cell and conforming to the $Fd\bar{3}m$ space group.

In recent years, an extensive number of researchers has focused on the AB_2S_4 type ternary sulfo-spinels among the class of chalco-spinels, due to their intriguing magnetic, electronic, and optical properties. In particular, the magnetic capacitance and refrigerant ability of chromium sulfo-spinel ($CdCr_2S_4$), known as a multiferroic material, have been the main subject of many experimental studies [22–24]. Additionally, in a computational study, the semiconducting behavior and dielectric properties of this sulfo-spinel were investigated by using the Hubbard potential within *ab initio* calculations [12]. Furthermore, the dielectric and charge transport properties of the antiferromagnetic $HgCr_2S_4$ cubic spinel system were investigated experimentally, and it was reported that this sulfo-spinel system is a multiferroic material with giant magnetocapacitance [7]. In this context, the main motivation of the present study is to bring a new member to the chalco-spinel family and to shed light on future experimental and theoretical research — such materials can be used in a wide variety of technological fields.

Our study presents the magnetic nature, semiconductivity and mechanical aspects of a silver-based chromium sulfo-spinel ($AgCr_2S_4$) system revealed with *ab initio* calculations utilizing a VASP package. The magnetic nature of this spinel system was determined to be ferromagnetic. Then, a spin-dependent electronic band structure was examined to obtain information about the electronic behavior in the ground state magnetic phase. Also, the mechanical stability and some elasticity properties of the $AgCr_2S_4$ sulfo-spinel were investigated. This new silver-based chromium sulfo-spinel was chosen for investigations, because many AB_2S_4 type ternary sulfo-spinel materials have a wide range of

uses in technology. The computational results obtained show that the related spinel compound has a semiconductor nature. Therefore, this compound could be a colossal nominee for spin-based electronic devices in technology.

2. Methodology of computations

To determine the magnetic nature, electronic and mechanical behavior of the presented sulfo-spinel system, computations under density functional theory (DFT) were performed with the Vienna Ab Initio Simulation Package (VASP) [25, 26] using the projector-augmented wave (PAW) method [27]. In the course of the computational DFT calculations, the Kohn–Sham equations were solved by the iteration approach [28]. The Perdew–Burke–Ernzerhof type pseudopotential based on the generalized gradient approximation (PBE-GGA) [29] and strongly constrained and appropriately normed semilocal density functional, meta-generalized gradient approximation (METAGGA-SCAN) [30] type pseudopotentials were adopted for exchange-correlation functionals. Along the calculations in this study, the valence states of Ag, Cr, and S atoms in the composition were treated as $5s^1 4d^{10}$, $3p^6 3d^5 4s^1$ and $3s^2 3p^4$, respectively.

During the structural optimization process leading to obtain the best suitable atomic locations and optimal structural parameters, the Brillouin zone integrations were achieved by an operated Monkhorst and Pack scheme with automatically generated $10 \times 10 \times 10$ k-point mesh yielding 110 k-points in the irreducible Brillouin zone [31]. For the electrons, the plane wave basis was chosen and with its help, the sets of system eigenfunctions were expanded up to the electron kinetic energy cut-off value equal to 800 eV. The Quasi-Newton method was used in order to minimize the force and pressure on the primitive cell and the optimization process was progressed until the forces on the ions were less than 10^{-8} eV/Å. The smearing criterion was applied on the fermionic occupation function as 0.01 eV using the Methfessel–Paxton type smearing. In order to find the iterative solution of the Kohn–Sham equations, the convergence parameter of energetic iteration steps was chosen as 10^{-9} eV. In this way, the most suitable Wyckoff positions for the ions in the primitive cell were obtained, with the pressure and force on the atoms set to zero.

3. Results and discussion

Firstly, the primitive cell of the silver-based chromium sulfo-spinel ($AgCr_2S_4$) was properly optimized by placing the ions in the most appropriate positions of the cell. Hence, optimized structural parameters were obtained with high accuracy. The primitive lattice of this sulfo-spinel system consists of 14 atoms and crystallizes in a face-centered cubic structure conforming to the $Fd\bar{3}m$ space group

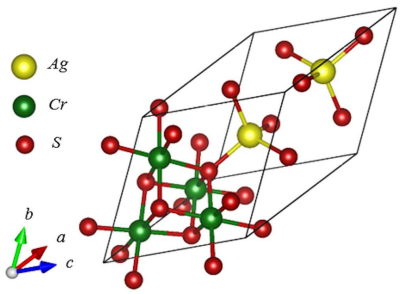

Fig. 1. The three-dimensional crystallized form of silver-based chromium sulfo-spinel $AgCr_2S_4$ in the primitive unit cell of fcc structure. The yellow, green, and red spheres represent Ag, Cr, and S atoms, respectively.

with the space number 227. In the optimized crystal, the Wyckoff positions of two Ag atoms and four Cr atoms were as 16d (0.5, 0.5, 0.5) and 8a (0.125, 0.125, 0.125), respectively, while eight S atoms were located at 32e (0.360, 0.360, 0.360). The illustration of the three-dimensional crystallographic form of the mentioned sulfo-spinel is presented in Fig. 1.

3.1. Determination of ground state magnetic phase

The three different types of magnetic phases for the related system in order to determine the ground state magnetic structure, i.e., antiferromagnetic (AFM), ferromagnetic (FM), and paramagnetic (PM) within GGA and METAGGA, have been considered. In the antiferromagnetic arrangement, the magnetic moments of the chromium (Cr) atoms were aligned antiparallel yielding a zero-net magnetization, while the magnetic moments of the atoms were oriented in the same direction for the ferromagnetic arrangement. The paramagnetic order was considered as a magnetic phase without spin effect. Then, the cohesive energies were calculated for each magnetic regulation. The cohesive energy is defined as the energy required to dissociate a crystal into free constituent atoms and can be calculated by using the total energy difference between the bulk crystal and isolated free atoms [32]. The structures with larger negative cohesive energy are more favorable energetically, while the system with positive energy cannot spontaneously emerge in nature.

The calculated cohesive energy values, the lattice parameters and atomic bond lengths for the system under consideration are given in Table I. For each magnetic phase considered, the calculated cohesive energies imply that the ferromagnetic phase is more stable energetically since the absolute value of the cohesive energy of this phase is greater than that of others. In this respect, the negative value of the calculated cohesive energy indicates that the silver-based chromium sulfo-spinel ($AgCr_2S_4$) is stable thermodynamically [33] so it can be synthesized at

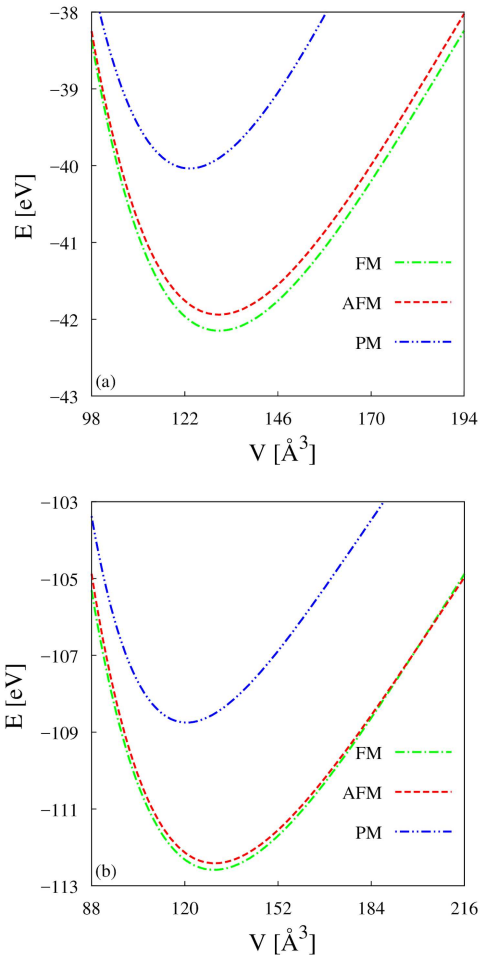

Fig. 2. The total energies of the primitive cell as a function of volume in FM, AFM, and PM orders within (a) GGA-PBE and (b) METAGGA of the $AgCr_2S_4$ sulfo-spinel.

ambient conditions to be technologically applicable. The energy-volume results for both approximations, which are obtained by fitting energy and volume data to the Vinet equation of states [34], are shown in Fig. 2. The energy–volume curves indicate clearly that the ground state phase of the system is ferromagnetic with the energy lower by $\approx$ 0.21 eV and $\approx$ 0.17 eV than the AFM phase for GGA and METAGGA, respectively. The PM phase has higher energies than both the FM and AFM phases, thus indicating an unfavorable crystal structure energetically. This result is exactly consistent with the calculated cohesive energies given in Table I.

The predominance of the Cr atoms is noticeable in the ferromagnetic nature of the mentioned system, as seen in Table II showing the computed partial magnetic moments. In addition, the fact that the total magnetic moment of this compound, which is obtained by using the METAGGA approximation, is close to the integer value emphasizes its semiconductor character. This will be discussed in the next subsection.

TABLE I

The lattice parameters (a in [Å]) and atomic bond lengths (d in [Å]) for the stable ferromagnetic phase and the calculated cohesive energies (E_{coh} in [eV]) of $AgCr_2S_4$ for the FM, AFM, and PM phases within GGA-PBE and METAGGA approximations.

Method	a [Å]	d_{Ag-S} [Å]	d_{Cr-S} [Å]	E_{coh} [eV]
GGA-PBE	7.178 (FM)	2.459 (FM)	2.397 (FM)	−27.563 (FM) −27.354 (AFM) −25.451 (PM)
METAGGA	7.142 (FM)	2.433 (FM)	2.391 (FM)	−24.616 (FM) −24.445 (FM) −20.782 (FM)

TABLE II

For GGA-PBE and METAGGA approximations, the calculated total magnetic moments μ_{tot} (in [μ_B]) of the ferromagnetic silver-based chromium sulfo-spinel ($AgCr_2S_4$) and the partial magnetic moments of Ag, Cr, and S atoms ($\mu_{Ag}, \mu_{Cr}, \mu_S$ in [μ_B]).

Method	μ_S [μ_B]	μ_{Ag} [μ_B]	μ_{Cr} [μ_B]	μ_{tot} [μ_B]
GGA-PBE	0.151	−0.081	2.752	9.639
METAGGA	−0.159	−0.100	2.888	10.083

TABLE III

For GGA-PBE and METAGGA approximations, the computed ground state energies for the antiferromagnetic E_{AFM} (in [eV]) and ferromagnetic E_{FM} (in [eV]) phases of the silver-based chromium sulfo-spinel $AgCr_2S_4$ and the predicted Curie temperatures T_C (in [K]).

Method	E_{AFM} [eV]	E_{FM} [eV]	T_C^{MFA} [K]
GGA	−41.940	−42.14	1616
METAGGA	−112.413	−112.584	1323

The Curie temperature (T_C) is a critical temperature where the spontaneous magnetization of the ferromagnetic system is lost due to thermal agitation effects. At this temperature, the ordered magnetic moments of a ferromagnetic material change and become disordered. In other words, the magnetic behavior of a material changes following a phase transition. The Curie temperature has a vital importance for systems having ferromagnetic nature and it can be roughly estimated from the ground state energy difference between the PM and FM phases by using the mean field approximation (MFA) [35–37]. The computed ground state energies for the antiferromagnetic and ferromagnetic phases of this sulfo-spinel and the predicted Curie temperatures according to the mean field approximation are given in Table III. The estimated Curie temperatures within the mentioned two methods for this sulfo-spinel are high, so it appears that the $AgCr_2S_4$ system is a strongly coupled ferromagnetic material.

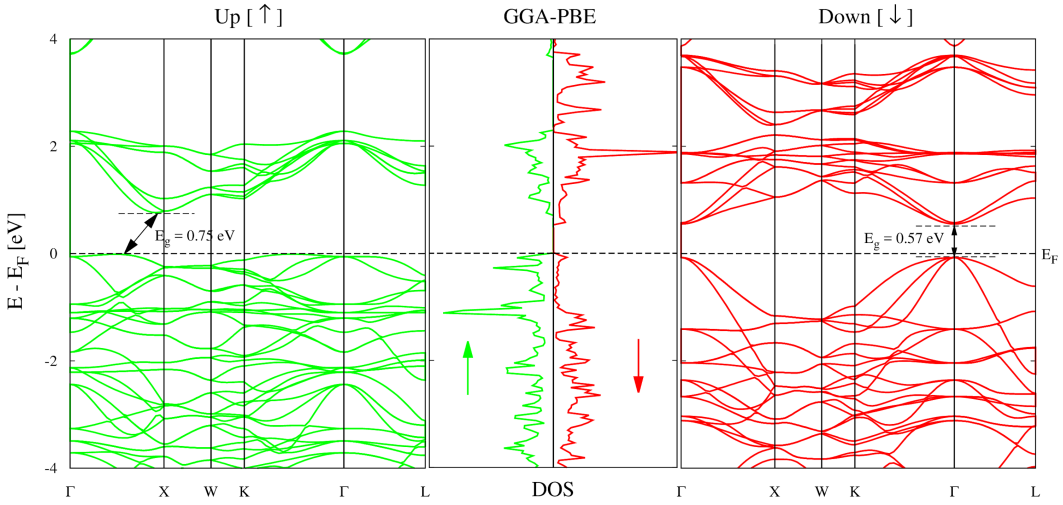

Fig. 3. The calculated spin polarized energy band structure with the total density of electronic states within GGA-PBE of sulfo-spinel $AgCr_2S_4$.

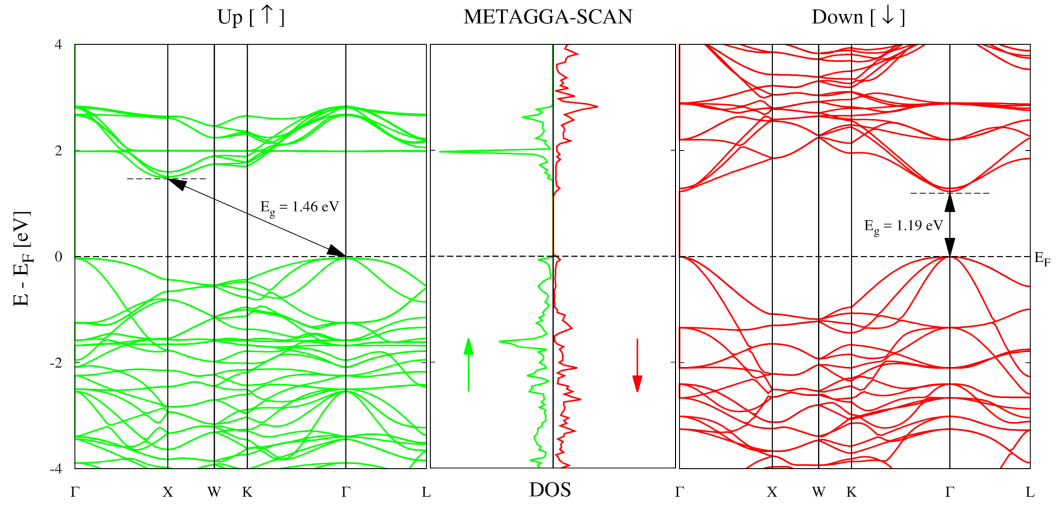

Fig. 4. Description used is the same as in Fig. 3, but within METAGGA-SCAN.

3.2. Observed electronic behavior in appropriate magnetic phase

After it was understood that this sulfo-spinel material has a ferromagnetic character in its ground state, the electronic band structure was examined under spin effect in order to discover its electronic behavior. In this regard, the spin-polarized energy band structure and the total density of electronic states of the system were calculated within GGA and constructed for minority and majority spin channels along the high-symmetry directions in the Brillouin zone, as shown in Fig. 3. This sulfo-spinel system can be classified as a semiconductor material due to band gaps in the majority ($E_g = 0.75$ eV) and minority ($E_g = 0.57$ eV) spin channels. The electronic behavior of the related compound was also observed with the METAGGA functional, as seen in Fig. 4. Moreover, the electronic band structure calculated with this approach showed a semiconductive character with larger band gaps ($E_g = 1.46$ eV for the majority spin channel and $E_g = 1.19$ eV for the minority spin channel). The fact that the band structures drawn for minority and majority spin channels differ from each other indicates that this material is not PM. This is consistent with the previous subsection where the magnetic nature of the material was discussed.

In order to understand the atomic projection of the semiconductor nature of the mentioned composition, the total (TDOS) and the orbital projected partial density of electronic states of atoms (PDOS) in this system were plotted within both calculation methods separately, as seen in Fig. 5. In Fig. 5a, the hybridizations between the d states of the Ag and Cr atoms and the $3p$ states of the S atoms are striking in the vicinity of the Fermi level (E_F). Below E_F, the $3d$ states of the Cr atoms around ≈ -1 eV are

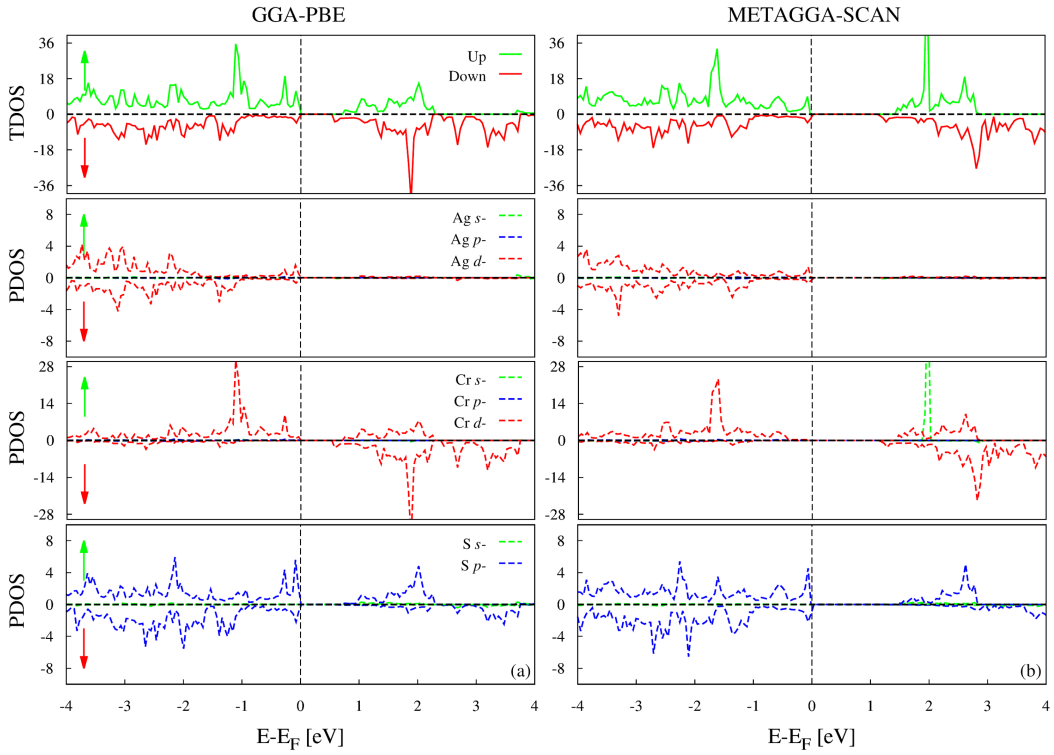

Fig. 5. The TDOS and orbital projected PDOS of atoms within (a) GGA-PBE and (b) METAGGA-SCAN of sulfo-spinel $AgCr_2S_4$.

dominant, while the $3p$ states of the S atoms in the valence band are effective in a wider energy range between 0 and -4 eV. Above E_F, i.e., in the conduction band, the d orbitals of the Cr atoms around ≈ 2 eV are dominant and there are hybridizations between d orbitals of the Cr atoms and p orbitals of the S atoms between 1.2 eV and 2.5 eV. It can be clearly understood that the bands around the Fermi level in the composition are mainly due to the d orbitals of the Cr atoms as well as the p orbital of the S atoms. Consequently, the semiconductor character of this spinel system can mainly be attributed to d-orbitals of chromium atoms and p-orbitals of sulphur atoms. Therefore, one can conclude that the s orbitals of atoms in this composition and p orbitals of the silver (Ag) and chromium (Cr) atoms have no effective dominance on the formation and chemical bonding properties of this composition. A similar statement is possible on the contribution of the orbitals of the elements to the TDOS, for the calculations made with another method — METAGGA. As seen in Fig. 5b, especially around the Fermi energy level, the dominance of the d-orbitals of the Cr atoms and the p-orbitals of the S atoms is striking.

3.3. Mechanical stability and elastic properties

The elastic constants of a solid have great importance in predicting the mechanical stability, flexibility, ductility, stiffness, compressibility, and even the type of atomic bond required for technological applications. In this part of the study, the stress-strain approximation [38] within the *ab initio* method was used to compute the second order elastic constants of this sulfo-spinel. It is known that a crystal having cubic symmetry has three independent elastic constants as C_{11}, C_{12} and C_{44} [39]. For the $AgCr_2S_4$ sulfo-spinel, the computed elastic stiffness constants according to the given approach are presented in Table IV.

TABLE IV

The computed elastic constants C_{ij} (in [GPa]) and the Cauchy pressure $C_p = C_{12} - C_{44}$ (in [GPa]) of $AgCr_2S_4$ by using the stress–strain approximation.

C_{11} [GPa]	C_{12} [GPa]	C_{44} [GPa]	C_p [GPa]
101.49	71.08	27.87	43.21

For technological applications, the resistance of a solid against compression should be known. Firstly, in this part of the research, it was examined whether the mentioned system has a mechanical stability. A cubic crystal can be regarded as mechanically stable, if its calculated elastic constants fulfill the Born–Huang criteria [39]. Since the elastic constants listed in Table IV satisfy the mentioned criteria, it can be concluded that this sulfo-spinel is mechanically stable. Furthermore, the brittleness or ductility of a crystal can be detected with the help of the computed Cauchy pressure [4]. If this pressure value $C_p = C_{12} - C_{44}$ is positive, then the crystal can be classified as a ductile material.

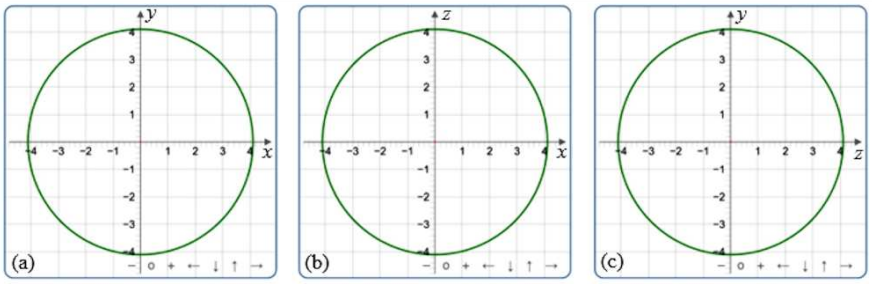

Fig. 6. The two-dimensional projections of linear compressibility β in (a) xy, (b) xz, (c) yz plane.

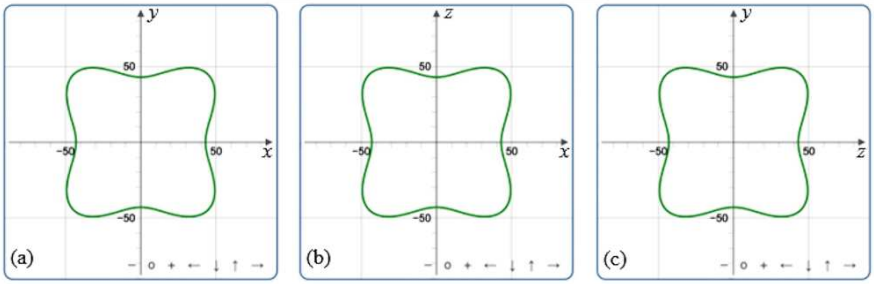

Fig. 7. Description used is the same as in Fig. 6, but for Young's modulus E.

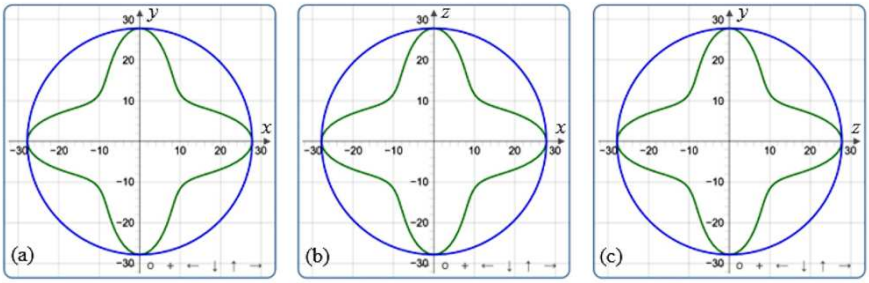

Fig. 8. Description used is the same as in Fig. 6, but for shear modulus G.

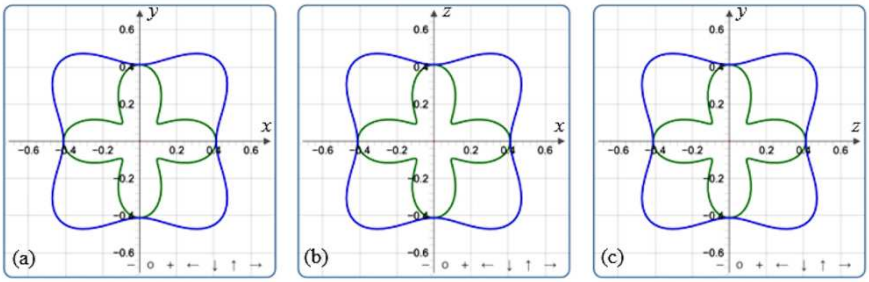

Fig. 9. Description used is the same as in Fig. 6, but for Poisson's ratio σ.

According to this assumption, this spinel structure is a ductile material. Therefore, it can be preferred for some industrial applications due to its ability to absorb relatively higher energy and to deform elastically.

The mechanical durability of a solid has great importance so that it could be grown on the substrate and turned into a device. In this regard, besides its electronic and magnetic behaviors, some mechanical properties of this system were also investigated. To explore some elasticity properties such as bulk (B), Young's (E) and shear (G) moduli, Pugh's (B/G) and Poisson's (σ) ratios, anisotropy shear factors (A and A^U), which are substantially important for a material, the previously computed elastic constants were used. For a crystal having cubic symmetry, the upper and lower limits of the shear modulus are different while the upper and lower limits of the bulk modulus are equal to each other. To calculate the upper and lower limits and the average value of shear modulus, the Voigt [41], Reuss [42] and Hill [43] approaches were used, respectively.

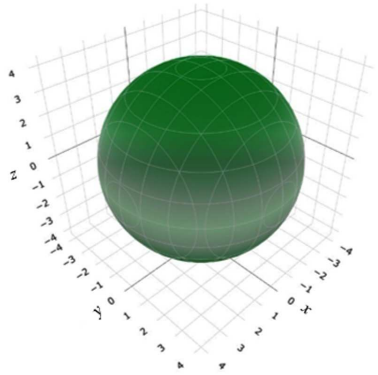

Fig. 10. The three-dimensional projections of linear compressibility β of $AgCr_2S_4$.

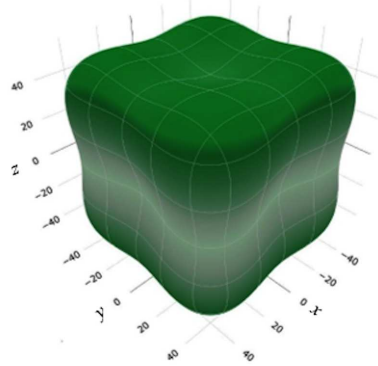

Fig. 11. Description used is the same as in Fig. 10, but for Young's modulus E.

TABLE V

The predicted bulk B (in [GPa]), Young's modulus E (in [GPa]) and shear modulus G (in [GPa]), Pugh's B/G and Poisson's σ ratios and anisotropy shear factors (A and A^U) for the sulfo-spinel $AgCr_2S_4$.

B	G_V	G_R	G_H	E	B/G	σ	A	A^U
81.22	22.80	20.90	21.85	60.17	3.716	0.377	1.833	0.454

TABLE VI

The calculated maximum and minimum values of Young's modulus (E_{min} and E_{max} in [GPa]), linear compressibility (β_{min} and β_{max}), shear modulus G (in [GPa]) and Poisson's ratio σ of ternary silver-based chromium sulfo-spinel ($AgCr_2S_4$).

E [GPa]		β		G [GPa]		σ	
E_{min}	E_{max}	β_{min}	β_{max}	G_{min}	G_{max}	σ_{min}	σ_{max}
42.93	75.02	4.10	4.10	15.20	27.87	0.13	0.61

The bulk modulus B is known as a measure of the resistance of a solid to external pressure [44]. The predicted relatively low bulk modulus for this sulfo-spinel indicates that this material can show weak resistivity to a volume change while a uniform hydrostatic pressure is applied on the system. The shear modulus G is known as a measure of the reversible deformation that occurs when shear stress is applied [44]. The predicted low value indicates that this compound is not much resistant to any shear deformation. Usually, the information on whether any material is stiff or not is obtained from Young's modulus E — defined as the ratio of stress and strain [45]. The calculated E shows that the investigated material has low stiffness. Therefore, it can be concluded that this compound is a soft and flexible material due to the predicted B, E and G values. Among the mechanical properties, Pugh's ratio can classify a solid as a ductile or brittle [44] material which is defined as the ratio of bulk modulus to shear modulus (B/G). According to the Pugh criterion, the ratio B/G must be > 1.75 in order to classify a solid as ductile. On the other hand, if the ratio is less than the critical value 1.75, the solid can be classified as brittle. The results given in Table V show that this sulfo-spinel system has very high ductility. The information about the compressibility of any solid crystal can be provided from its Poisson's ratio (σ) [45]. When, for a given material, σ is close to 0.5 value, it can be said that it has an incompressible nature [45]. As seen in Table V, the mentioned ratio calculated for this system is 0.377 and this indicates that one deals with almost a compressible material. Also, Poisson's ratio can be used to get information about the bonding type between the atoms in a crystal. For crystals with covalent type bonds this ratio should be around 0.1 and for crystals with ionic type bonds [46] it should be 0.25. According to this assumption, the atomic bonding type between the atoms of this composition is nearly ionic.

As the mechanical properties of the sulfo-spinel $AgCr_2S_4$ have been discussed, finally, the anisotropy shear factor [47], one of the mechanical parameters of this compound, was calculated since it has the ability to determine elastic anisotropy of a solid crystal. Furthermore, the universal anisotropy factor (A^U) [48], which should be zero for an isotropic crystal, was calculated from the upper and lower limits of bulk and shear modulus.

As presented in Table V, the calculated anisotropy shear factors for the ternary silver-based chromium sulfo-spinel ($AgCr_2S_4$) imply its relatively high anisotropic nature. Also, in order to better understand and visualize the anisotropic behavior of this compound depending on the direction, two- and three-dimensional linear compressibility, shear modulus, Young's modulus, and Poisson's ratio were obtained from the EIAM code [49] with the use of the calculated elastic constants. For the mentioned mechanical parameters of the silver-based chromium sulfo-spinel, the obtained two-dimensional projections depending on planes, and the obtained three-dimensional projections depending on crystallographic directions are presented in Figs. 6–13. The maximum and minimum values

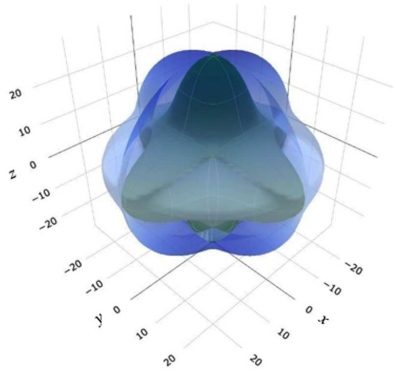

Fig. 12. Description used is the same as in Fig. 10, but for shear modulus G.

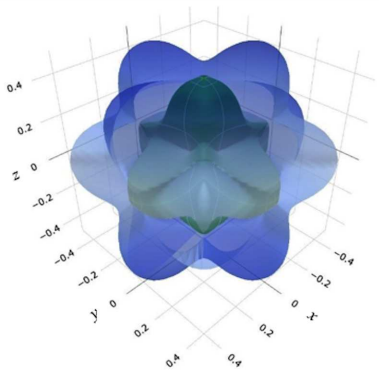

Fig. 13. Description used is the same as in Fig. 10, but for Poisson's ratio σ.

of the related mechanical parameters of this sulfo-spinel are given in Table VI. For a solid crystal to be isotropic mechanically, it is known that especially these three-dimensional images must be spherical, otherwise if the material is not isotropic, these images will deviate from a spherical shape [50, 51]. As shown in Figs. 6 and 10, the investigated compound exhibits an isotropic behavior in terms of compressibility, thus, indicating its high ductility. However, when looking at the two- and three-dimensional projections of other parameters, it becomes more clear that the anisotropic nature of this material is dominant.

4. Conclusion

In this theoretical study, we performed comprehensive *ab initio* calculations to reveal the magnetic nature, electronic behavior, and mechanical stability with elastic properties of the ternary silver-based chromium $AgCr_2S_4$ sulfo-spinel crystallizing in a face-centered cubic structure which conforms to the $Fd\bar{3}m$ space group and 227 space number. The ferromagnetic phase was determined to be the most suitable phase for this compound since the ground state energy of this magnetic phase was less than those of others in view of the calculated equation of states for three different types of magnetic orders. This situation is confirmed by the calculated cohesive energy.

The calculated electronic band structures within the GGA-PBE and METAGGA-SCAN approaches showed that the electronic character of this sulfo-spinel system was semiconductor since there are band gaps in the majority spin (E_g = 0.75 eV for GGA-PBE and E_g = 1.46 eV for METAGGA-SCAN) and the minority spin (E_g = 0.57 eV for GGA-PBE and E_g = 1.19 eV for METAGGA-SCAN) channels. Therefore, the investigated material is a promising candidate for spintronic applications since it has semiconductor and ferromagnetic characteristics and is able to provide a fully-spin polarized current. Furthermore, this compound has mechanical stability due to satisfying the Born–Huang criteria and it is a ductile material. In this regard, $AgCr_2S_4$ can be used in several technological applications since the ductile materials are able to absorb more elastic energy than brittle ones.

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