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The electronic and elasticity properties of new half-metallic chalcogenides Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te): an *ab initio* study

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ABSTRACT

The ternary copper-based chalcogenides Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te), which have simple cubic (SC) crystal structure and conform to $P\bar{4}3m$ space group with 215 space number, have been investigated by spin-polarised generalised gradient approximation (GGA) in the framework of density functional theory (DFT). All systems have been considered in ferromagnetic (FM) order. The mechanical and thermal properties and the electronic band structures of these systems have been investigated after the well-optimised structural parameters have been obtained. The spin-polarised electronic band structures of all the systems exhibit half-metallic behaviour with band gaps in minority spin channel from 0.29 eV for Cu_3FeTe_4 to 1.08 eV for Cu_3CrS_4 , while metallic band structures are observed for majority spins. This agrees with the calculated total magnetic moments which are close to integer values. The calculated negative formation enthalpies indicate the energetic and thermodynamic stability of these compounds. Moreover, the calculated elastic constants verify that these materials are stable mechanically due to satisfying Born stability criteria. The estimated anisotropy shear factors show that Cu_3FeS_4 , Cu_3FeSe_4 and Cu_3CrSe_4 systems have nearly isotropic character with 1.004, 0.910, and 0.958 values, respectively, whereas other compounds have relatively low anisotropic behaviour.

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Half-metallic; electronic structure of bulk materials; mechanical properties of solids; density functional theory; chalcogenides

1. Introduction

The ternary copper-based chalcogenide compounds, e.g. sulphides, selenides and tellurides, are much interesting materials with intriguing physical properties and good candidates for wide range of industrial applications for optoelectronic devices such as PV cells, light modulators or thermoelectrics. Therefore, they

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have been attracting considerable attention both experimentally and theoretically in the past few years [1–6]. Cu_3MCh_4 type chalcogenides, in which M atoms can be usually chosen from transition metals (TM), have simple cubic (SC) crystal structure which conforms to $P\bar{4}3m$ space group with 215 space number [7,8] and there are several reports about their preparation and synthesis procedure in literature [9–13].

In some earlier works, authors have studied Cu_3MCh_4 type sulphides and selenides systems and found that these compounds belong to the *p*-type semiconductors family [14–16]. Another work on optical properties of Cu_3VS_4 compound in the cubic sulvanite structure shows that the photoconductive properties of this material are stable even at high temperatures up to 250°C [17]. In an experimental study, researchers focused on Cu_3TaSe_4 thin films with a smaller band gap ($E_g = 2.35$ eV) to be used in multi-junction solar cells [18]. Apart from those studies, it has been presented theoretically that ternary Cu_3MCh_4 (M = Sb, Bi and Ch = S, Se) chalcogenides are good candidates for solar cell absorbers [19]. In another theoretical work on the electronic properties of sulvanite structured semiconductors Cu_3MCh_4 (M = V, Nb, Ta and Ch = S, Se, Te), authors conclude that these materials are very suitable for optoelectronic applications [20].

In this study, we have examined the electronic band structures, mechanical, and thermo-elastic behaviours of copper-based chalcogenide systems Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) which crystallise in the simple cubic (SC) sulvanite structure and belong to $P\bar{4}3m$ space group. Since these materials have possible applications in spintronic with half-metallic band gaps, the addition of new materials to ternary copper-based chalcogenide series is important. To the best of our knowledge, these compounds in cubic structural phase have not been investigated yet in detail. There are only a few works on Cu_3FeS_4 compound in bornite-idaite structural phase in literature [21,22]. Also, it is important to know the electronic and mechanical behaviours of these compounds in cubic crystal structure. The obtained results show that they can be used in spintronic applications just like other new chalcogenides which have half-metallic character due to small band gaps observed in the minority (down) spin channel in their electronic band structures. Besides, the electronic behaviour of these interesting materials, their mechanical and thermodynamic stabilities can be much important for technological applications. In this context, we have carried out a detailed ab-initio analysis of copper-based Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide compounds by using VASP code. The calculation methods are presented in the next section. The obtained structural parameters, the calculated elastic constants, the electronic band structures with the density of states (DOS) and some thermal parameters are given in the third section. Finally, we have concluded and summarised our results in the last section.

2. Computational details

For all the calculations in this study, we have used VASP (Vienna Ab initio Simulation Package) [23,24] software with projector augmented wave (PAW) method [25]. For all atoms in the compositions Perdew, Burke and Ernzerhof (PBE) [26] type pseudopotentials have been considered to approximate exchange–correlation potential within the framework of generalised gradient approximation (GGA) of density functional theory (DFT) in which Kohn–Sham equations are solved numerically and iteratively [27,28]. The valence electron configurations of *Cu*, *Cr*, *Fe*, *S*, *Se* and *Te* atoms in the compositions are as follows: $3d^{10}4s^1$, $3d^54s^1$, $3d^74s^1$, $3s^23p^4$, $3d^{10}4s^24p^4$, and $4d^{10}5s^25p^4$.

Brillouin zone integrations have been performed with automatically generated $12 \times 12 \times 12$ k-point mesh in the irreducible Brillouin zone yielding 56 k-points following the Monkhorst Pack scheme [29]. For basis sets expansion of the wave functions, the kinetic energy cut-off value has been chosen as 1000 eV which is large enough to describe the physical properties in great accuracy. Methfessel–Paxton type smearing method has been applied on fermionic occupation function with 0.01 eV smearing width. For the ionic relaxation process, the quasi-Newton method has been applied until the forces on ions are less than 10^{-8} eV/Å. Also, the convergence criterion for energy in successive iteration steps has been taken 10^{-9} eV. The lattice parameters and atomic positions of atoms in primitive cell of the crystals have been well optimised by minimising both the forces and the pressure on these systems.

3. The obtained results

Firstly, we have relaxed Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide compounds to obtain well-optimised structural parameters and suitable atomic positions in the primitive cell. In the primitive cell of this type of crystal, three Cu atoms are positioned on the Wyckoff positions 3d (0.5, 0, 0), transition metal (TM) atom (Cr or Fe) is placed on 1a (0, 0, 0), whereas four chalcogenides (S, Se, Te) are placed at 4e ((0.232, 0.232, 0.232) for Cu_3CrS_4 , (0.239, 0.239, 0.239) for Cu_3CrSe_4 , (0.247, 0.247, 0.247) for Cu_3CrTe_4 , (0.228, 0.228, 0.228) for Cu_3FeS_4 , (0.245, 0.245, 0.245) for Cu_3FeSe_4 , and (0.255, 0.255, 0.255) for Cu_3FeTe_4) as seen in [Figure 1](#). The three-dimensional (3D) crystallographic representation of these compounds, which are in simple cubic ($P43m$ space group with space number 215) phase with 8-atom primitive cell, is shown in [Figure 1](#). After the structural relaxation process are completed, optimal structural parameters have been obtained. Then, electronic band structures, mechanical stability, and also some elastic and thermal properties have been examined by using these optimised parameters.

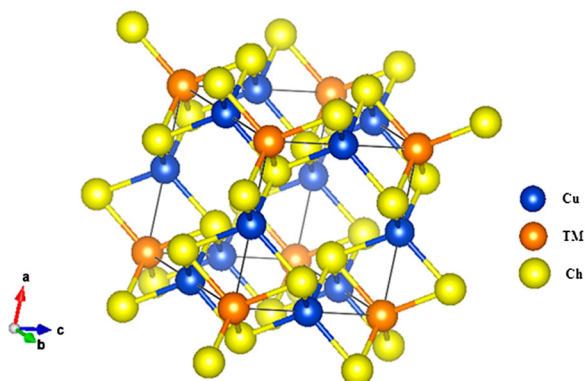


Figure 1. The three dimensional (3D) crystallographic shape of ternary copper chalcogenides Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te). The blue, orange and yellow coloured atoms represent copper ions, transition metal ions, and chalcogen anions, respectively.

3.1. The optimised structural parameters and the thermodynamic stability

The obtained structural parameters, e.g. lattice constants, bond lengths and the formation enthalpy values which are important to decide thermodynamic stability, have been tabulated in Table 1 for Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide compounds. The formation enthalpy (ΔH_f) of a crystal which has the chemical formula A_xB_y , can be calculated from its internal energy changes [30] as seen in Equation (1),

$$\Delta H_f = E_{tot} - (xE_A^{bulk} + yE_B^{bulk}), \quad (1)$$

where E_{tot} is the total energy of the unit cell of the crystal. E_A^{bulk} and E_B^{bulk} are the ground state energy values of A and B atoms in their bulk crystal forms. Due to this definition, if the calculated formation enthalpy of a crystal is negative, this crystal is thermodynamically stable or is structurally synthesisable. The calculated negative formation enthalpy values given in Table 1 indicate that these compounds are thermodynamically stable and synthesisable materials for technological applications.

After obtaining ground state volume and energy values of these materials, energy-volume curves are plotted as seen in Figure 2 by fitting the Vinet

Table 1. The optimised lattice parameters, bond lengths, and the calculated formation enthalpies of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) (Space group: $P43m$, Space No:215) chalcogenides.

Material	a (Å)	$d_{\text{TM-Ch}}$ (Å)	$d_{\text{Cu-Ch}}$ (Å)	ΔH_f (eV/f.u.)
Cu_3CrS_4	5.440	2.19444	2.30730	-8.561
Cu_3CrSe_4	5.661	2.34394	2.41787	-4.591
Cu_3CrTe_4	5.976	2.55914	2.57827	-0.838
Cu_3FeS_4	5.483	2.15597	2.30158	-7.798
Cu_3FeSe_4	5.593	2.38048	2.40898	-4.330
Cu_3FeTe_4	5.880	2.60137	2.56533	-1.092

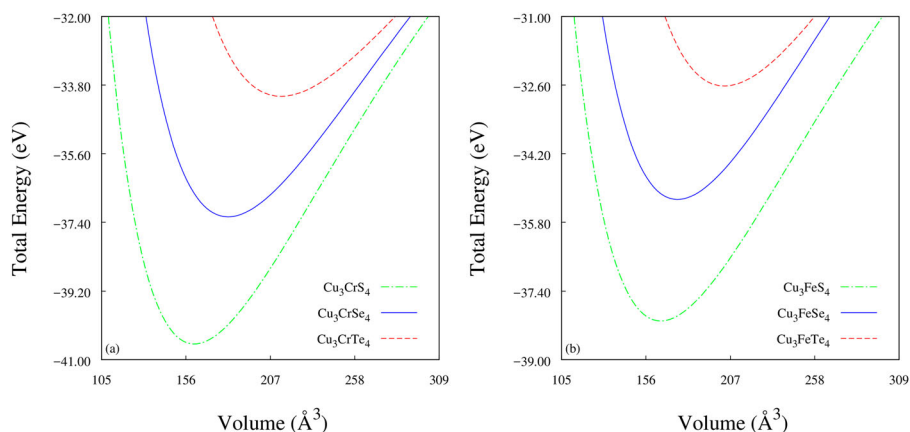


Figure 2. Total energies of primitive cell as a function of volume of ternary copper chalcogenides: (a) Cu_3CrCh_4 (Ch = S, Se, Te), (b) Cu_3FeCh_4 (Ch = S, Se, Te).

equation of state [31]. A well-converged ground state is obtained for each of our materials, with the asymptotic standard errors in fitting process being less than about 1%. The calculated lattice parameters with fitting process are given in Table 1.

As seen in Table 1 and in Figure 2, the energetic stability of Cu_3CrS_4 compound is the highest, while Cu_3CrTe_4 compound has lowest stability. Also, it can be clearly seen that sulphur atoms increase the energetic stability whereas tellurium atoms decrease. There is not any available study in literature about these systems, which are crystallised in the simple cubic (SC) crystal structure, to make a comparison. Moreover, it is obviously seen that TM-Ch and Cu-Ch bond lengths are increased in tellurides compared to sulphides indicating higher energetic stability.

3.2. The calculated electronic band structure and magnetic moments

The electronic behaviour of a crystal can be described with the calculated electronic band structure and the density of states (DOS) which can give more and detail information. The calculated spin-polarised electronic band structures and the total density of states (DOS) of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenides within GGA have been plotted for both majority (up) and minority (down) spin channels along the high symmetry lines in the first Brillouin zone as seen in Figures 3 and 4. It is clearly seen from the figures that these materials have half-metallic character, since there are minority (down) spin band gaps which are $E_g = 1.08$ eV for Cu_3CrS_4 , $E_g = 1.04$ eV for Cu_3CrSe_4 , $E_g = 1.01$ eV for Cu_3CrTe_4 , $E_g = 0.31$ eV for Cu_3FeS_4 , $E_g = 0.50$ eV for Cu_3FeSe_4 , $E_g = 0.29$ eV for Cu_3FeTe_4 . All the observed band gaps are indirect gaps which are from R to X point for Cu_3CrCh_4 and Cu_3FeSe_4 systems, from R to M point for Cu_3FeTe_4 system, and from R to Γ

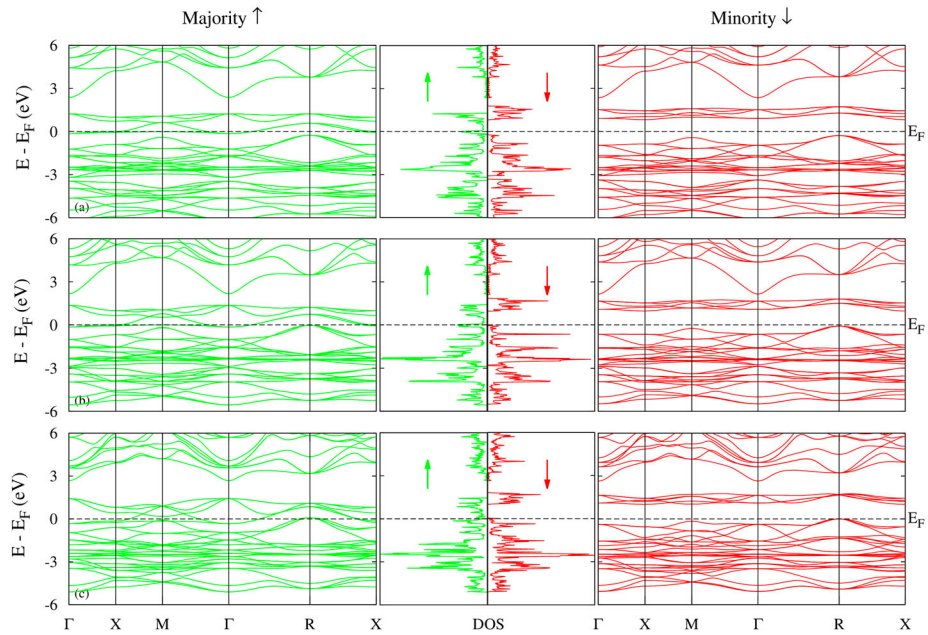


Figure 3. The calculated energy band structures and the total density of electronic states (DOS), within GGA for (a) Cu_3CrS_4 , (b) Cu_3CrSe_4 , (c) Cu_3CrTe_4 . The zero of band energy is shifted to Fermi level (E_F).

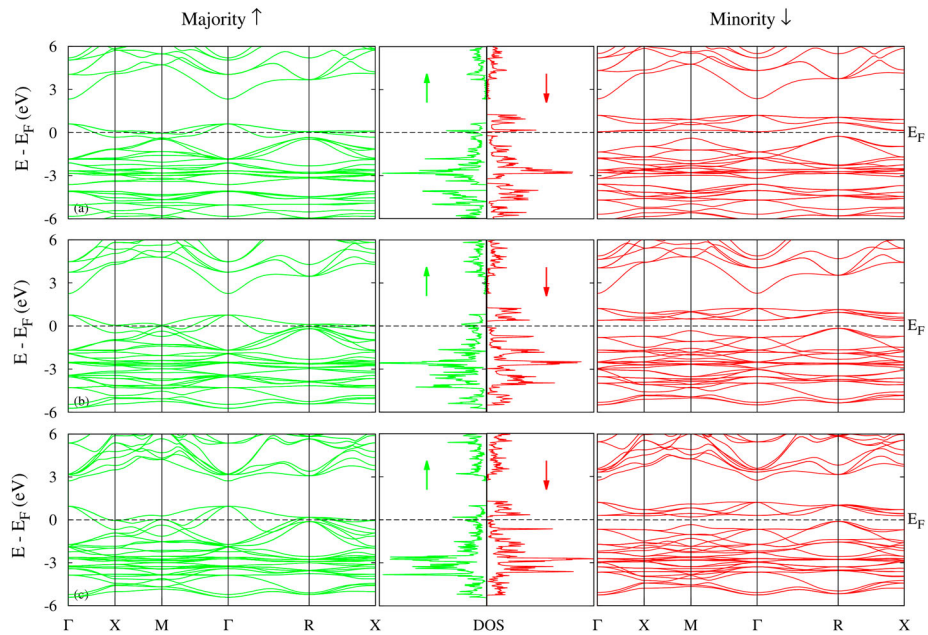


Figure 4. The calculated energy band structures and the total density of electronic states (DOS), within GGA for (a) Cu_3FeS_4 , (b) Cu_3FeSe_4 , (c) Cu_3FeTe_4 . The zero of band energy is shifted to Fermi level (E_F).

point for Cu_3FeS_4 . Also, the distribution of majority and minority spin channels are nonsimilar which indicates that the magnetic characters of our systems are not paramagnetic.

The calculated orbital projected partial density of electronic states of Cu_3CrCh_4 and Cu_3FeCh_4 ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$) compounds are presented in Figures 5 and 6, respectively. There are hybridisations between $3d$ states of transition metal atoms (Cu , Cr , and Fe) and p -orbitals of chalcogen atoms (S , Se and Te) (between -2 eV and -3 eV) in the valence band which is below Fermi level and also between $3d$ states of Cr (Fe) and p -orbitals of chalcogenides (S , Se , and Te) (around 1.5 eV) in the conduction band which is above Fermi level. Below the Fermi level, Cu - d states (almost -3 eV) are dominant for all materials while Cr (Fe)- d states (almost 1.5 eV) are dominant above the Fermi level for these systems, as seen in Figures 5–6, respectively. Also, there are Cr - d states (around -1 eV and -2.5 eV) below the Fermi level for Cu_3CrCh_4 compounds and there are Fe - d states (around -0.5 eV and -5 eV) below the Fermi level for Cu_3FeCh_4 compounds, as seen in Figures 5–6, respectively. Additionally, it can be seen that filled- $3d$ ($4d$) states of Se (Te) atoms in selenides (tellurides) have no remarkable effect on bonding features of Cu_3TMSe_4 and Cu_3TMTe_4 material series. The electronic states around Fermi level can only contribute to bonding between the atoms and the low energy states corresponding to closed shell electrons have no effect on bonding behaviour. As seen in Figure 5, d -states of Se and Te atoms

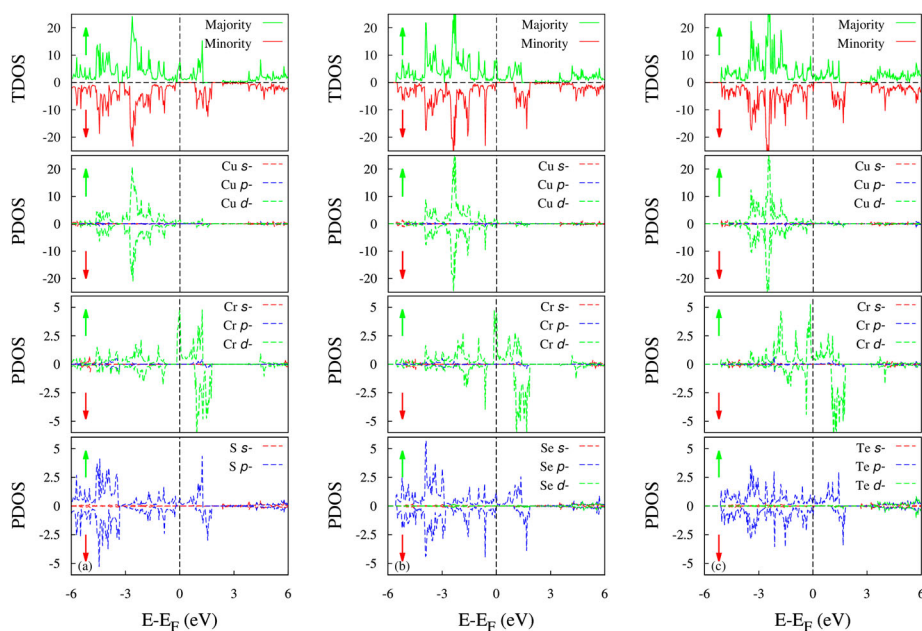


Figure 5. The total and orbital projected partial density of electronic states of atoms within GGA for (a) Cu_3CrS_4 , (b) Cu_3CrSe_4 , (c) Cu_3CrTe_4 .

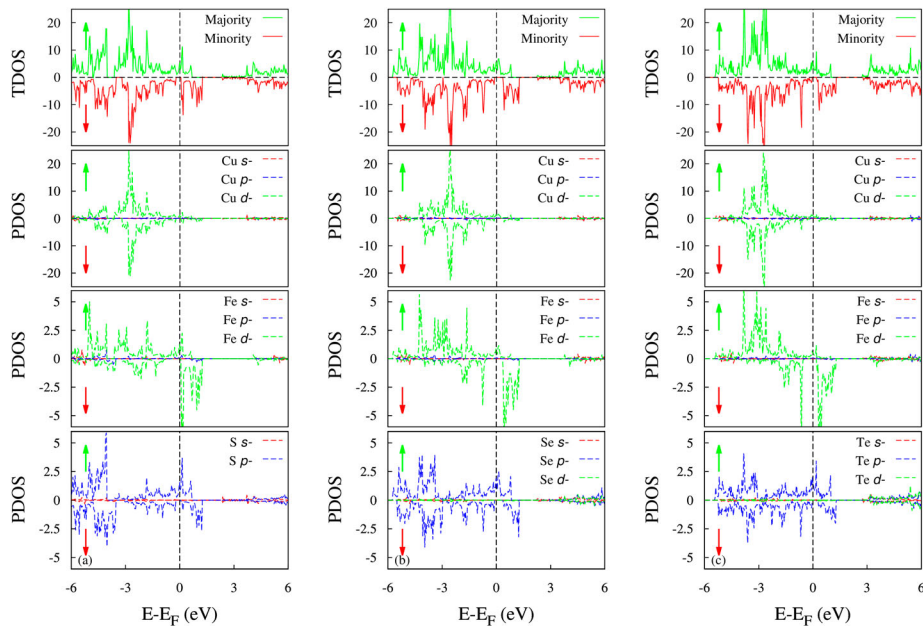


Figure 6. The total and orbital projected partial density of electronic states of atoms within GGA for (a) Cu_3FeS_4 , (b) Cu_3FeSe_4 , (c) Cu_3FeTe_4 .

(dashed green lines) have very low density of states around Fermi level. That means these states have not a determining role in bonding and the formation of related crystal phase. In this view, half-metallicity and the bonding properties of these systems are mainly determined by d -orbitals of transition metal atoms (Cu , Cr , and Fe) and p -orbitals of chalcogen atoms (S , Se , and Te) and hybridisations between them. These compounds can be regarded as half-metallic and can be used in spintronic devices.

Our materials have ferromagnetic nature due to the plotted energy-volume graphs in antiferromagnetic and ferromagnetic phases by using GGA within DFT, as seen in Figure 7. For all materials in this study, a $2 \times 2 \times 2$ super-cell which is composed of 64 atoms, is used to calculate energy and volume values. The calculated values have been fitted to Vinet equation of state [31]. We have obtained a well-converged ground state for all compounds in this study due to the asymptotic standard errors about 1 % in fitting the Vinet equation.

The partial magnetic moments of Cr (Fe) atoms play a dominant role on the total magnetic moment of these systems. Therefore, Cr (Fe) atoms are responsible for the ferromagnetic nature of these compounds, as tabulated in Table 2. Also as a typical property of half-metallic materials, total magnetic moments of these chalcogenides are close to the integer values; especially $\mu_{\text{Cu}_3\text{CrS}_4} = 0.990 \mu_B$, $\mu_{\text{Cu}_3\text{CrSe}_4} = 1.036 \mu_B$.

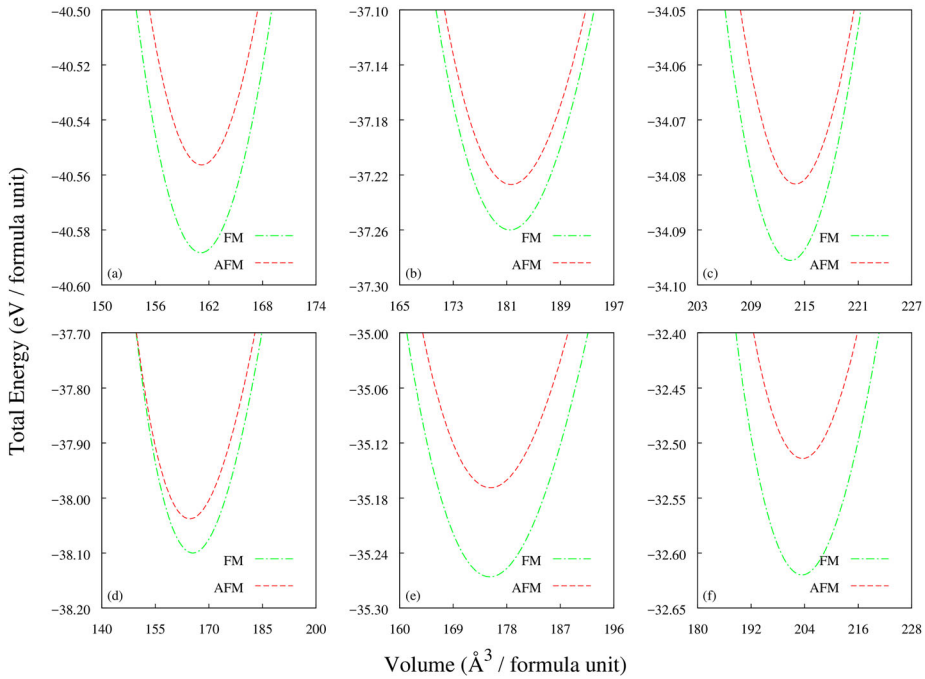


Figure 7. Total energies as a function of volume in antiferromagnetic and ferromagnetic phases of (a) Cu_3CrS_4 , (b) Cu_3CrSe_4 , (c) Cu_3CrTe_4 , (d) Cu_3FeS_4 , (e) Cu_3FeSe_4 , and (f) Cu_3FeTe_4 .

3.3. The mechanical stability and the estimated mechanical properties

We have used ‘stress–strain’ approximation [32] within *ab initio* method to calculate the elastic constants of these compounds. Then, the mechanical stability and elasticity have been examined with these constants. The calculated elastic constants of a solid can give more and detailed information about the dynamical behaviours such as mechanical stability, hardness or brittleness even bonding types of a crystal. For a crystal having cubic symmetry, it is well known that there are three independent elastic constants which are C_{11} , C_{12} and C_{44} [33] and the calculated second-order elastic constants of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenides within first principles methods are presented in Table 3.

In technological applications, the mechanical stability or the durability of a crystal against external forces is a desirable feature. In this view, the calculated elastic constants of a crystal must satisfy some criteria well known as the Born-Huang mechanical stability criteria in order to be mechanically stable [33]. For any cubic crystal, these criteria depending on the calculated elastic constants are given by

$$C_{11} - C_{12} > 0; C_{11} + 2C_{12} > 0; C_{11} > 0 \text{ and } C_{44} > 0. \quad (2)$$

Table 2. The calculated total magnetic moments (μ_B) of the ternary copper-based chalcogenides Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) in ferromagnetic order and total magnetic moments of Cu, Cr, and, Fe atoms and also chalcogenides (S, Se and Te) in compositions.

Material	$\mu_{\text{tot}}(\mu_B)$	$\mu_{\text{atom}}(\mu_B)$
Cu_3CrS_4	0.990	$\mu_{\text{Cu}} = -0.079$ $\mu_{\text{Cr}} = 1.212$ $\mu_{\text{S}} = -0.143$
Cu_3CrSe_4	1.036	$\mu_{\text{Cu}} = -0.149$ $\mu_{\text{Cr}} = 1.431$ $\mu_{\text{Se}} = -0.246$
Cu_3CrTe_4	1.156	$\mu_{\text{Cu}} = -0.208$ $\mu_{\text{Cr}} = 1.751$ $\mu_{\text{Te}} = -0.387$
Cu_3FeS_4	2.723	$\mu_{\text{Cu}} = 0.149$ $\mu_{\text{Fe}} = 2.362$ $\mu_{\text{S}} = 0.212$
Cu_3FeSe_4	2.790	$\mu_{\text{Cu}} = 0.007$ $\mu_{\text{Fe}} = 2.712$ $\mu_{\text{Se}} = 0.071$
Cu_3FeTe_4	2.802	$\mu_{\text{Cu}} = 0.001$ $\mu_{\text{Fe}} = 2.813$ $\mu_{\text{Te}} = -0.012$

Table 3. The calculated second-order elastic constants and Cauchy pressures (C_p) of copper-based chalcogenides Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) within GGA approximation.

Material	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	C_p (GPa) = $C_{12} - C_{44}$
Cu_3CrS_4	72.40	24.62	17.34	7.28
Cu_3CrSe_4	53.06	22.73	14.53	8.20
Cu_3CrTe_4	36.86	19.71	13.31	6.40
Cu_3FeS_4	63.03	24.93	19.13	5.80
Cu_3FeSe_4	52.56	19.05	15.25	3.80
Cu_3FeTe_4	38.82	17.24	13.83	3.41

The calculated second-order elastic constants within ‘stress–strain’ approximation show that these materials are stable mechanically since their calculated elastic constants satisfy these stability criteria.

Among the elastic constants of a cubic crystal, elastic modulus C_{44} gives information about resistance to shear deformation across the (100) plane in the [110] direction and tetragonal shear constant $(C_{11} - C_{12})/2$ value presents resistance to deformation by shear on the (110) plane in the $[1\bar{1}0]$ direction [34–36]. It is clearly seen that C_{44} constants and $(C_{11} - C_{12})/2$ values of tellurides are lower than the others indicating the weakness of the telluride systems to shear deformation along these directions, whereas sulphides have higher strength to shear deformation in the same directions.

The Cauchy pressure which can be calculated as $C_p = C_{12} - C_{44}$, can give information about the ductility or brittleness of a crystal [37]. The crystal is regarded as ductile when the calculated Cauchy pressure is positive. On the contrary, the Cauchy pressure of brittle materials is negative. These chalcogenides are ductile with positive Cauchy pressure values, this is a desired property in

industrial applications, since brittle materials are not able to absorb energy and do not deform plastically and therefore, show tendency easily fracture under stress and strain [38]. Among the compounds under investigation, the ductility of Cu_3CrSe_4 is more evident than the other as seen in Table 3.

3.3.1. The estimated elastic properties

We used the calculated elastic constants to predict some important elastic properties of these chalcogenides; such as bulk (B) and shear moduli (G), Young's modulus (E), Poisson's ratio (σ) and Pugh's ratio (B/G). The Voigt [39] and Reuss [40] approximations present upper (B_V , G_V) and lower limits (B_R , G_R) of bulk (B) and shear moduli (G) of a crystal as in Equations (3)–(5), respectively. Also, average value bulk (B) and shear moduli (G) can be calculated by using Hill (B_H , G_H) [41] approximation which is a measure of resistance to reversible deformations upon shear stress and represents the resistance to plastic deformation as in Equation (6). It is well known that B_V , B_R and B_H values of a cubic crystal are equal to each other.

$$B_V = B_R = B_H = (C_{11} + 2C_{12})/3, \quad (3)$$

$$G_V = (C_{11} - C_{12} + 3C_{44})/5, \quad (4)$$

$$G_R = 5(C_{11} - C_{12})C_{44}/(4C_{44} + 3C_{11} - 3C_{12}), \quad (5)$$

$$B_H = (1/2)(B_V + B_R) \text{ and } G_H = (1/2)(G_V + G_R). \quad (6)$$

In addition, Young's modulus (E) [42] which can determine the linear strain along edges of a crystal and is given as the ratio of stress and strain, and Poisson's ratio (σ) [42] which can give detailed information about the compressibility of a crystal, can be predicted by using bulk and shear moduli as given in Equations (7) and (8), respectively.

$$E = (9BG)/(3B + G), \quad (7)$$

$$\sigma = (3B - 2G)/[2(3B + G)]. \quad (8)$$

The estimated Young's modulus (E) which we have used to characterise stiffness of our materials, indicate that these compounds can be regarded as soft materials, as presented in Table 4. Among the materials, sulphides are stiffer materials than

Table 4. The estimated bulk modulus, shear moduli, Young's moduli, Poisson's ratios, Pugh's ratios (B/G) of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide materials.

Material	B (GPa)	G_V (GPa)	G_R (GPa)	G_H (GPa)	E (GPa)	B/G	σ
Cu_3CrS_4	40.55	19.96	19.48	19.72	50.90	2.056	0.291
Cu_3CrSe_4	32.84	14.79	14.77	14.78	38.56	2.221	0.304
Cu_3CrTe_4	25.43	11.42	10.91	11.16	29.21	2.278	0.309
Cu_3FeS_4	37.63	19.10	19.10	19.10	49.01	1.970	0.283
Cu_3FeSe_4	30.22	15.85	15.82	15.83	40.44	1.908	0.277
Cu_3FeTe_4	24.44	12.61	12.43	12.52	32.09	1.952	0.281

the others whereas telluride chalcogenides have higher flexibility. The predicted bulk moduli (B), shear modulus (G_V , G_R and G_H), Young's modulus (E), B/G (Pugh's ratio) and Poisson's ratios (σ) of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenides within *ab initio* methods are tabulated in Table 4.

The ductility of the solid materials can be predicted from the calculated B/G value which is known as Pugh's ratio [43]. The brittle and ductile materials can be separated from each other by the critical value known as 1.75. If the calculated Pugh's ratio of a crystal is lower than this critical value, it can be said about this material as a brittle whereas the ductile materials have higher Pugh's ratio. In this respect, our compounds in this work are ductile materials and also, the Cauchy pressure (C_p) calculations in Section 3.3 are compatible with this prediction.

The nature of incompressible or compressible character of any crystal can be understood from the predicted Poisson's ratio (σ). If this ratio approximates to 0.5 ($\sigma \rightarrow 0.5$) the material tends to be incompressible behaviour and the material can be regarded nearly incompressible while this value is equal to 0.5 ($\sigma = 0.5$) [44]. It is clearly seen from Table 4 that the calculated Poisson's ratios of these compounds are around 0.3 which shows that our materials have nearly compressible in nature.

The shear anisotropy factor which can be defined as a measure of the degree of the elastic anisotropy of a material, is an important mechanical parameter for solids. A cubic crystal has two shear anisotropy factors which are A for the $\{100\}$ planes and A_- for the $\{110\}$ planes and also can be calculated as given in Equations (9) and (10), respectively [45]:

$$A = 2C_{44}/(C_{11} - C_{12}), \quad (9)$$

$$A_- = C_{44}(C_L + 2C_{12} + C_{11})/(C_L C_{11} - C_{12}^2), \quad (10)$$

whereas $C_L = C_{44} + (C_{11} + C_{12})/2$.

The A_- value for the $\{110\}$ planes of a crystal which has cubic symmetry, is not independent of A , but does reduce to A for conditions of elastic isotropy as $2C_{44} = C_{11} - C_{12}$. The predicted shear anisotropy factors for our materials in this study are tabulated in Table 5. These calculated values indicate that Cu_3FeS_4 , Cu_3FeSe_4 and Cu_3CrSe_4 compounds have nearly isotropic character with 1.004, 0.910 and 0.958, respectively, whereas other compounds show low

Table 5. The calculated anisotropy shear factors (A and A_-) of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide materials.

Material	A for the $\{100\}$ planes	A_- for the $\{110\}$ planes
Cu_3CrS_4	0.726	0.781
Cu_3CrSe_4	0.958	0.968
Cu_3CrTe_4	1.552	1.371
Cu_3FeS_4	1.004	1.003
Cu_3FeSe_4	0.910	0.931
Cu_3FeTe_4	1.282	1.199

anisotropic character mechanically and also anisotropic behaviour of these materials for (100) plane are greater than that for (110) plane.

3.3.2. The estimated some thermal properties

Among the fundamental parameters of a crystal, Debye temperature (θ_D) is related to plasticity and thermal properties, such as elastic constants, specific heat and melting temperature. Furthermore, the high and low-temperature regions of solid crystals can be roughly defined with this parameter, since a higher Debye temperature indicates a higher thermal conductivity and melting temperature. In this study, Debye temperatures (θ_D) of these compounds have been estimated by the following formula [46],

$$\theta_D = (h/k)[(3n/4\pi)(N_A\rho/M)]^{1/3}v_m, \quad (11)$$

where h is the Planck's constant, ρ is the density of the material, k the Boltzmann's constant, N_A is the Avogadro's number, M is the molecular weight, n is the number of atoms in the molecule and finally v_m is the average wave velocity. The predicted Debye temperatures (θ_D) of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenides are given in Table 6. The calculated values show that sulphur atoms increase Debye temperature value of the compound whereas tellurium atoms reduce.

The sound conductivity nature of a solid can be predicted with the calculated wave velocities such as average (v_m), longitudinal (v_l) and transverse (v_t) wave velocities which are also necessary parameters to calculate Debye temperature. The average wave velocity (v_m) can be calculated using the following expression [46]:

$$v_m = \{(1/3)[(2/(v_t^3)) + (1/(v_l^3))]\}^{-1/3}. \quad (12)$$

The longitudinal wave velocity (v_l) and the transverse wave velocity (v_t) of a crystal can be obtained from Navier's equation [47] as presented below.

$$v_l = [(B + (4G/3))/\rho]^{1/2}, \quad (13)$$

$$v_t = [G/\rho]^{1/2}. \quad (14)$$

The calculated wave velocities of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide systems are tabulated in Table 6. It is clearly seen that, in sulphide

Table 6. The calculated longitudinal (v_l), transverse (v_t), and average (v_m) wave velocities and also Debye (θ_D) and melting temperatures (T_{Melt}) of Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenide materials.

Material	v_l (m/s)	v_t (m/s)	v_m (m/s)	θ_D (K)	T_{Melt} (K)
Cu_3CrS_4	4181.6	2271.2	2533.9	263.1	981 ± 300
Cu_3CrSe_4	3206.7	1700.8	1900.8	192.9	867 ± 300
Cu_3CrTe_4	2622.8	1380.2	1543.3	149.7	771 ± 300
Cu_3FeS_4	4056.9	2232.1	2487.8	257.8	926 ± 300
Cu_3FeSe_4	3103.0	1723.4	1919.5	197.2	864 ± 300
Cu_3FeTe_4	2580.1	1423.5	1586.3	156.4	782 ± 300

type chalcogenides, sound velocity values are higher than in the selenide and telluride type chalcogenides, like Debye temperatures (θ_D) values. Therefore, it can be said that the sound conductivity of sulphides is better than that of other types.

Now, we have roughly predicted the melting temperature (T_{Melt}) from the calculated C_{11} constants of our compounds by following the formula [48]

$$T_{Melt} = \left[553 \text{ K} + \left(\frac{5.91 \text{ K}}{\text{GPa}} \right) C_{11} \right] \pm 300 \text{ K} \quad (15)$$

It can be seen from Table 6 that, the roughly estimated melting temperatures of these compounds are in accordance with Debye temperature values. To the best of our knowledge, there are no available data in literature to make a meaningful comparison.

4. Conclusion

In this study, the thermodynamic and mechanical stability, electronic band structures with the calculated magnetic moments, and some thermal properties of copper-based Cu_3TMCh_4 (TM = Cr, Fe and Ch = S, Se, Te) chalcogenides which conform to $P\bar{4}3m$ space group with 215 space number, have been investigated in detail. The compositions have been evaluated in ferromagnetic order. The calculated formation enthalpies show that the chosen compounds are thermodynamically stable and synthesisable materials for technological applications. Due to GGA band structures, all the materials have half-metallic character due to minority indirect band gaps which are $E_g = 1.08$ eV for Cu_3CrS_4 , $E_g = 1.04$ eV for Cu_3CrSe_4 , $E_g = 1.01$ eV for Cu_3CrTe_4 , $E_g = 0.31$ eV for Cu_3FeS_4 , $E_g = 0.50$ eV for Cu_3FeSe_4 , $E_g = 0.29$ eV for Cu_3FeTe_4 with nearly integer magnetic moments. All materials in this study have mechanical stability due to the calculated elastic constants satisfying Born-Huang criteria and are ductile with positive Cauchy pressure. Also, the predicted anisotropy shear factors indicate that especially Cu_3FeS_4 , Cu_3FeSe_4 and Cu_3CrSe_4 systems have nearly isotropic character with 1.004, 0.910 and 0.958, respectively, whereas other compounds indicate low anisotropic behaviour. The present alloys with especially half-metallic electronic band structures can be good candidate for spintronic devices and also with ductility can be used in technological applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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