

First Principles Study of the New Half-metallic Ferromagnetic Full-Heusler Alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$: An Ab-initio Study

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Abstract We present an ab-initio study of the structural, electronic, elastic, magnetic, thermal and thermodynamic property of the quaternary Heusler alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ ($x = 0, 0.25, 0.5, 0.75, 1$) with the linearized augmented plane wave method based on density functional theory (DFT) and implemented in WIEN2k code. For exchange correlation potential we have used the generalized gradient approximation (GGA) of Perdew et al. Our results provide a theoretical study for the mixed Heusler $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ ($0 < x < 1$) in which no experimental or theoretical data are currently available. In their equilibrium $L2_1$ structure, all concentrations are equilibrium $L2_1$ structure; all concentrations are magnetic and metallic. However, there is linear variation of the lattice parameter. The bulk modulus, the elastic constants and the Debye temperature was studied with variation of composition x of Ge. A regular solution model is used to investigate the thermodynamic stability of the alloy which is essentially shows a miscibility gap phase by calculating the critical temperatures of the alloys. In addition, the quasi-harmonic Debye model is applied to determine the thermal properties of the alloy.

Keywords DFT, FP-LAPW Method, WIEN2k, Half-metallic, Heusler, Ferromagnetic

1. Introduction

The history of a class of new materials can be traced back to the year 1903, Fritz Heusler alloy discovered that a type of formula Cu_2MnAl behaves like a ferromagnetic material, although its components are not the magnetic materials in them same [1, 2]. The history of a class of new materials can be traced back to the year 1903, Fritz Heusler alloy discovered that a type of formula Cu_2MnAl behaves like a ferromagnetic material, although its components are

not the magnetic materials in them same [1, 2].

Half-metallic ferromagnets (HMFs) have been intensively investigated during the last decade because of their potential application in spintronics devices [3]. With the development of spintronic devices in the recent years, materials with complete spin polarization at the Fermi level E_F have attracted much attention because they are of great interest for scientific research and industrial applications [3–5]. Important classes of materials which are at present under intense study are the so-called half-metals [6]. Heusler alloys are a very interesting class of compounds as they are known to display various appealing properties such as magneto resistance, thermoelectric and shape memory effect etc. They have been nicely summarized in a comprehensive review [7]. These materials are hybrids between metals and semiconductors or insulators, presenting metallic behavior for one spin band and semiconducting for the other, and thus overall they are either ferro- or ferrimagnets with perfect spin-polarization at the Fermi level [8]. Groot and his collaborators in a pioneering paper published in 1983 predicted the existence of half-metallicity in the case of the intermetallic Heusler alloy NiMnSb [9].

The Heusler ternary alloys are determined by the generic formulas X_2YZ or XYZ [10, 11], The X_2YZ Heusler alloys (X_2YZ) where X and Y are transition metals, and Z is an element of group III, IV or V, in some cases, Y is replaced by either a rare earth element. The X_2YZ Heusler compounds crystallize in the cubic $L2_1$ (AlCu_2Mn -type) structure with the space group $Fm-3m$. In this structure, X, Y and Z atoms are placed on the Wyckoff positions 8c ($1/4, 1/4, 1/4$), 4a (0, 0, 0) and 4b ($1/2, 1/2, 1/2$), respectively. The cubic X_2YZ compounds can also be found in the CuHg_2Ti type structure. This formal $XYXZ$ -type structure exhibits Td symmetry with the space group $F-43m$. In that structure the two X atoms occupy nonequivalent positions in contrast to the $L2_1$ structure. This structure is frequently observed when the nuclear charge of the Y element is

larger than the one of the X element from the same period, that is $Z(Y) > Z(X)$ for two 3d transition metals. In this structure, X atoms occupy the nonequivalent 4a (0, 0, 0) and 4c (1/4, 1/4, 1/4) positions, while Y and Z atoms are located on 4b (1/2, 1/2, 1/2) and 4d (3/4, 3/4, 3/4) Wyckoff positions, respectively [12]. The alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ these is new innovative material for many application spinotronic, these alloys have a special interest because of their relatively high Curie températeur.

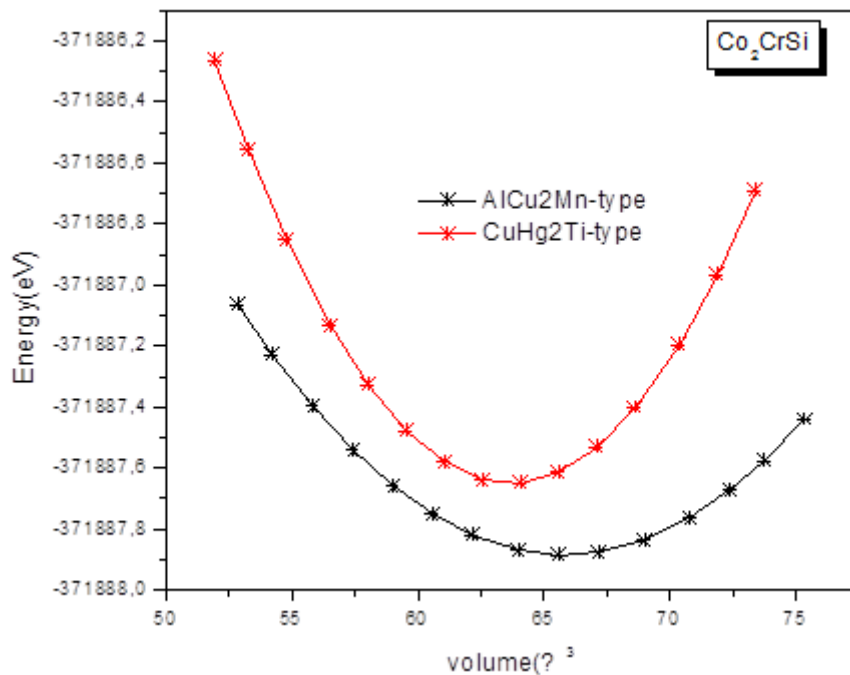
2. Calculation Methodology

This study is performed using density functional theory DFT [13] calculations within the framework of full-potential linearized augmented plane-wave (FP-LAPW) method as implemented in WIEN2k package [14, 15]. The generalized-gradient approximation (GGA) is used for the exchange correlation potential [9]. The muffin-tin sphere radii RMT were chosen as equal to 2.1, 2.3, 1.7 and 2.2 a.u for the Co, Cr, Si and Ge atoms, respectively. The plane wave cut-off parameter is taken as $\text{RMT} \cdot K_{\text{max}} = 8.5$, the Brillouin zone sampling was performed according to the Monkhorst–Pack scheme and for k-space integration, a (14 * 14 * 14) mesh was used resulting in 104k points of the irreducible part in the Brillouin zone [14]. Study of thermodynamic properties was performed within the quasi-harmonic Debye model implemented in the Gibbs program [15]. The quasi-harmonic Debye model allows us to obtain all thermodynamics quantities from the calculated energy-volume points. Detailed descriptions of this procedure can be found in Refs. [15-19].

3. Results and Discussion

3.1. Structural Properties

In the first step, we present the results for the geometrical structure of the quaternary Heusler alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ as well as the lattice parameter and bulk modulus. To obtain the equilibrium lattice constant and determine the stable structure of these alloys, we perform structural optimizations on Co_2CrSi and Co_2CrGe alloys for nonmagnetic (NM), magnetic (M) and configurations for both AlCu_2Mn -type ($L2_1$) and CuHg_2Ti -type structures. It is clearly seen that these structures are more stable in the AlCu_2Mn -type ($L2_1$) than in the CuHg_2Ti -type (see Fig. 1). The calculated total energies versus volume are fitted to the empirical Murnaghan's equation of state [20] to determine the ground state properties. For Co_2CrSi in the AlCu_2Mn -type structure, the second step of our calculations was to study the structural properties of the quaternary Heusler alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$, we use in the present study the minimal super cells compatible with the percentage of constituents in question. The lattice structures have been modeled at some selected compositions $x = 0.25, 0.5$ and 0.75 . For the considered structures, we perform the structural optimization by minimizing the total energy with respect to the cell parameters and also to the atomic positions. Our calculated lattice constants at different compositions, as shown in Table 1, were found to vary almost linearly following Vegard's law [21] with marginal downward bowing parameters equal to 0.00697 \AA . The bulk modulus decreases on going from Co_2CrSi to Co_2CrGe and increases slightly showing a non-linear behavior.



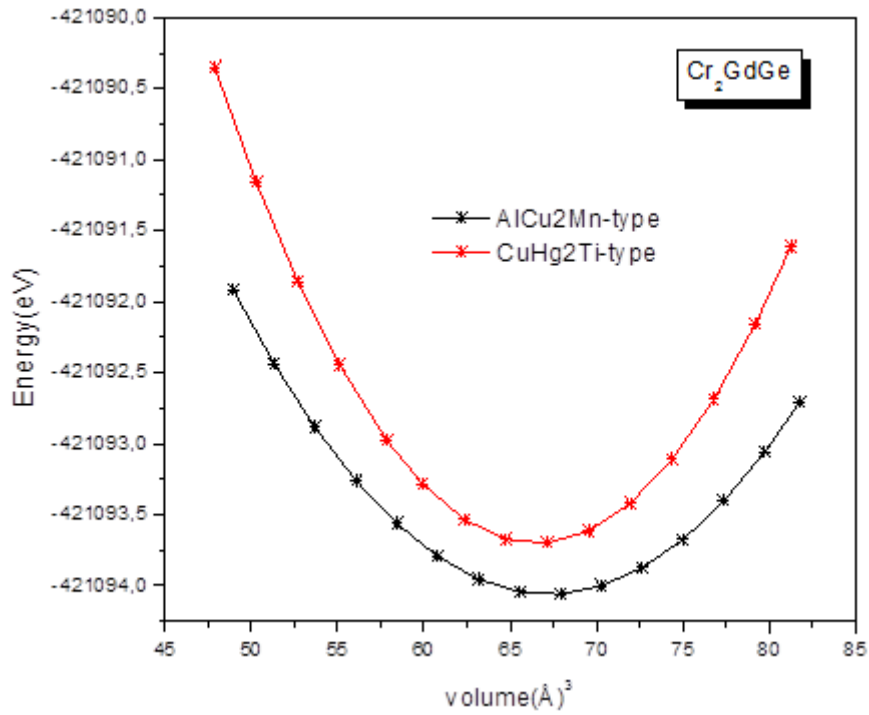
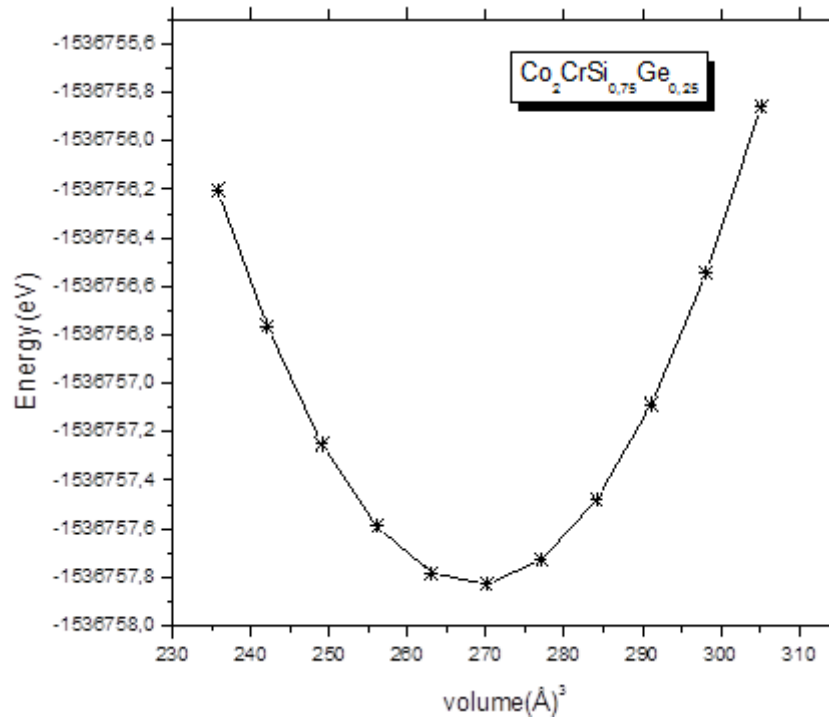


Figure 1. Calculated total energy versus volume curves ferromagnetic (FM) state for AICu₂Mn-type and CuHg₂Ti-type phases of Co₂CrSi and Co₂CrGe



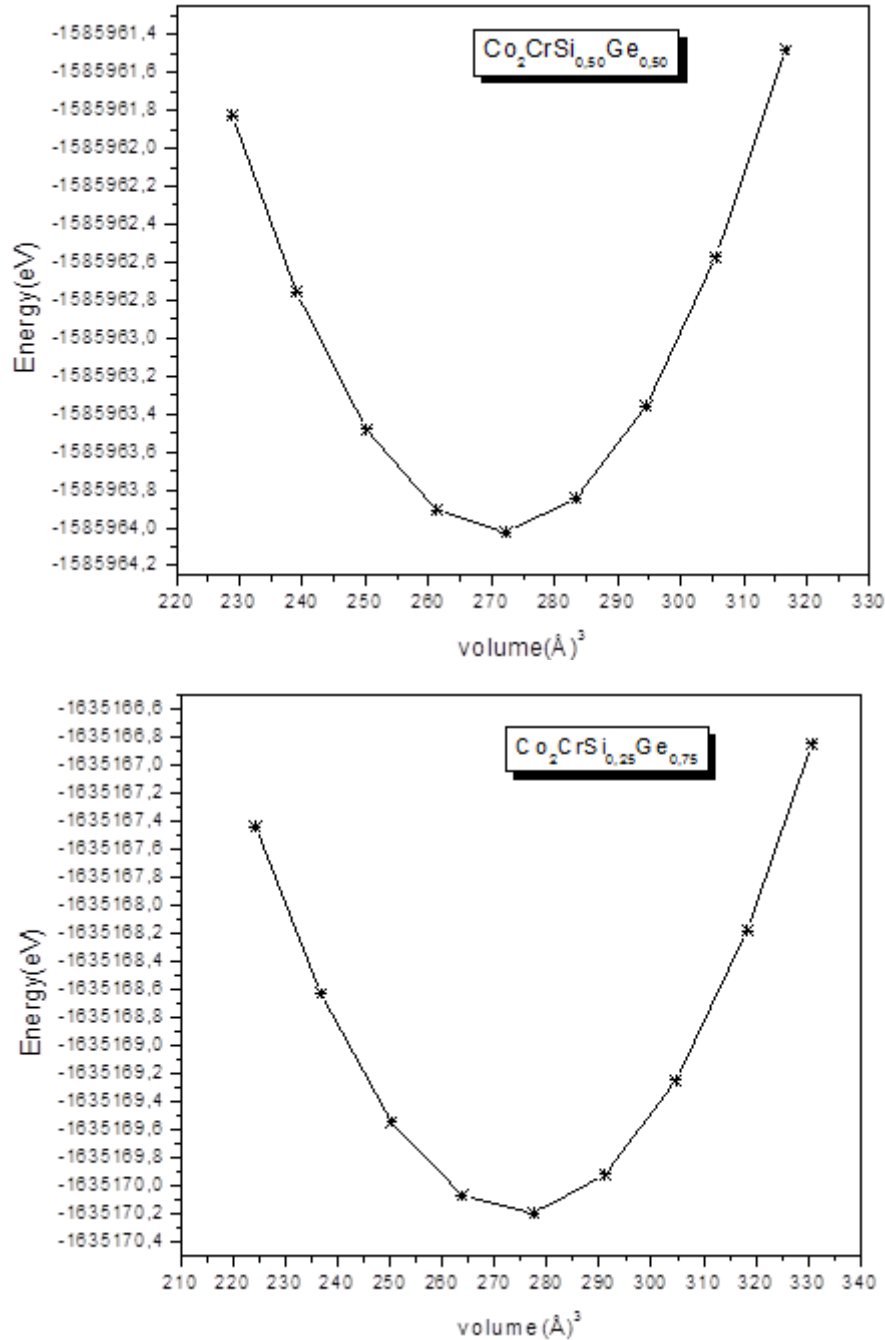


Figure 2. Variation of the total energy as a function of volume for $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ alloys, a) $x = 0.25$, b) $x = 0.5$, c) $x = 0.75$.

3.2. Elastic Properties

The elastic constants are important parameters for describing the mechanical properties of materials that undergo stress, and give important information concerning the binding characteristic between adjacent atomic planes, anisotropic character of binding and structural stability. There are independent elastic constants, C_{ij} , but the symmetry of cubic crystal reduces this number to only three independent elastic constants C_{11} , C_{12} and C_{44} .

In Table 1, the calculated three independent elastic constants C_{11} , C_{12} and C_{44} , shear modulus G , ratio of

B/G , Young's modulus E , Poisson's ratio (μ), Zener anisotropy factor (A), density (ρ), longitudinal elastic wave velocities v_l , transverse elastic wave velocities v_t , average acoustic velocity v_m , and Debye temperature (θ_D) of $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ for various compositions are listed. To our knowledge, we note that no result regarding the elastic constants are so far available in the literature. The traditional mechanical stability conditions in cubic crystals at equilibrium are expressed in terms of elastic constants as follows: $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{12} < B < C_{11}$ [22]. The computed elastic constants satisfy the above stability criteria, indicating that these compounds are

elastically stable. The variation of the elastic constants works as a function of composition x. It is seen that, the elastic constants C₁₁, C₁₂, C₄₄ decreases monotonically with x, the alloy structure becomes mechanically stable.

The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. Our obtained values for Poisson's ratio vary from 0.369 to 0.372, which is an indication that the interatomic forces are central forces [23]. From our calculated values of the Zener anisotropy factor A, which is a measure of the degree of elastic anisotropy of the crystal, we note that our Heusler alloys are elastically isotropic

The Young's modulus E and Poisson's ratio m are important in technological and engineering application [24]. Young's modulus is defined as the ratio of stress and strain when Hooke's law holds. The Young's modulus of a material is the usual property used to characterize stiffness. The higher the value of E, the stiffer is the material. From Table 1, the Young's modulus decreases when we move from 0 to 1. Thus, the Co₂CrSi is stiffer than Co₂CrGe. The Debye temperature is known to be an important fundamental parameter closely related to many physical properties, such as specific heat and melting temperature. At low temperatures, the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements.

Table 1. Calculated lattice constant (a), bulk modulus (B), pressure derivative of the bulk modulus (B'), elastic constants (C_{ij}), shear modulus (G), ratio of B/G, Young's modulus (E), Poisson's ratio (ν), zener anisotropy factor (A), density (ρ), longitudinal elastic wave velocities (V_l), transverse elastic wave velocities (V_t), average acoustic velocity (V_m), and Debye temperature (θ_D) of Co₂CrSi_{1-x}Ge_x for various compositions

	Co ₂ CrSi _{0.75} Ge _{0.25}	Co ₂ CrSi _{0.50} Ge _{0.50}	Co ₂ CrSi _{0.25} Ge _{0.75}
a(Å)	6.4021	6.4192	6.4401
B (Gpa)	116.9321	114.8143	111.7985
B'	4.1243	4.3630	4.1957
C ₁₁ (GPa)	255.9906	246.3009	234.6867
C ₁₂ (GPa)	147.6590	139.3190	135.5527
C ₄₄ (GPa)	50.2373	47.2059	44.2890
G(Gpa)	51.0087	48.9197	45.6002
B/G	3.5045	3.4756	3.5839
E(GPa)	144.2141	138.3910	129.6495
ν	0.3697	0.3687	0.3723
A	0.9643	0.9198	0.9338
ρ(g/cm ³)	4.2892	4.5104	4.7209
V _l (m/s)	7543.6908	7187.8559	6867.8643
V _t (m/s)	3375.1800	3223.3224	3042.2204
V _m (m/s)	3907.0055	3739.2980	3545.6822
θ _D (K)	354.1048	334.0897	312.4310

Fig 3 shows the variation of the lattice parameter calculated based on the concentration of germanium for the quaternary alloy. A slight deviation from the Vegard's law is clearly visible for the alloy with bowing upwardly parameter equal to 0.0024 Å, obtained by adjusting the values calculated by a polynomial function. The physical origin of this small gap could be mainly due to the low disparity Co₂CrSi of lattice constants and ternary

compound Co₂CrGe. The equation that represents the variation of the lattice parameter depending on the concentration of Germanium is:

$$A=6.2049+0.3910x+0.0024x^2$$

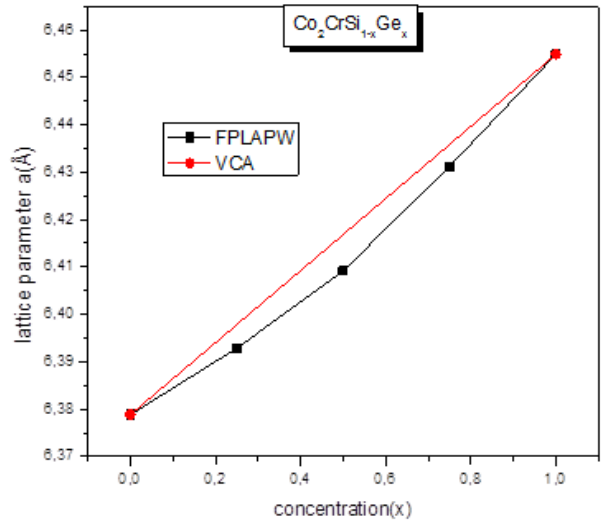


Figure 3. Variation of the lattice parameter of Co₂CrSi_{1-x}Ge_x Heusler alloys with Ge concentration.

Fig 4 represents the variation of the bulk modulus as a function of the germanium concentration in the Co₂CrSi_{1-x}Ge_x alloy. A significant deviation of the bulk modulus is observed with a disorder parameter equal to 8.243 GPa for Co₂CrSi_{1-x}Ge_x alloys, show that the incompressibility modulus decreases with increasing the concentration of Ge (0 ≤ x ≤ 1). The equation that represents the compressibility modulus of variation depending on the concentration of Germanium is:

$$B=192.8820-40.6745x+8.2430x^2$$

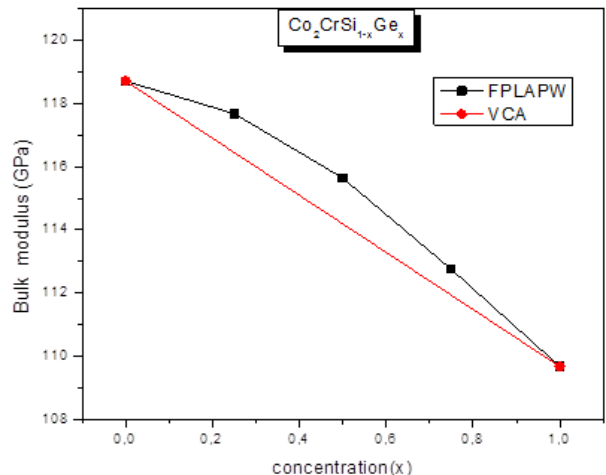


Figure 4. Variation of the Bulk modulus of Co₂CrSi_{1-x}Ge_x Heusler alloys with Ge

3.3. Electronic Properties

To elucidate the nature of the electronic band structure, we also calculated the total and partial densities of states, as shown in Figures 6 most transport properties are

determined on the basis knowledge of the density of states. Generally, in the vicinity of the Fermi level, the bands are mainly due to orbital states d of Cr and the transition metals; this is justified by the half metallic character.

Densities of states confirming the metallic character for the majority of densities are presented in Figure 5. A lack of electronic states at the Fermi level of minority spins us closer to the semiconductor and semi-metallic character for both alloys. From Figure 6, it is clear that there are three distinct regions in the spin-up state and in the spin-down state separated by gaps materials.

We notice an overlap valence and conduction bands to the state spin-up, while the existence of electronic states at the Fermi level tells us about the nature of these metal alloys. The presence of electronic states is most obvious for the spin up, it is minimal for the spin down and shows the near character semiconductor, and in this state we see a gap between the conduction and the valence band. It can be said that the compounds and their alloys are semiconductors in the state spin-dn. This means that the system has a half-metallic character. We notice a change in indirect gap for quaternary alloy materials studied.

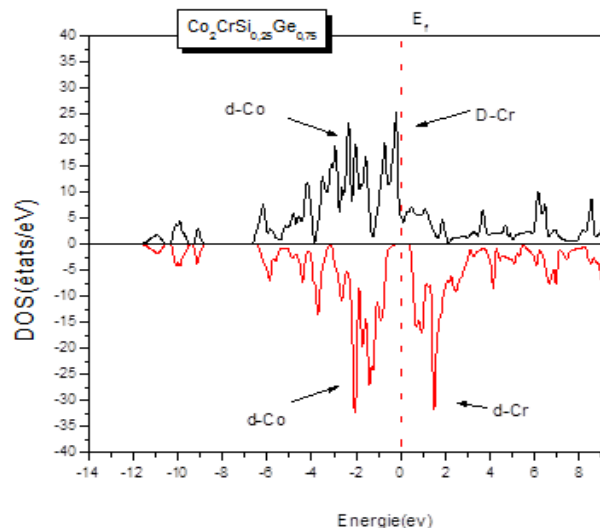
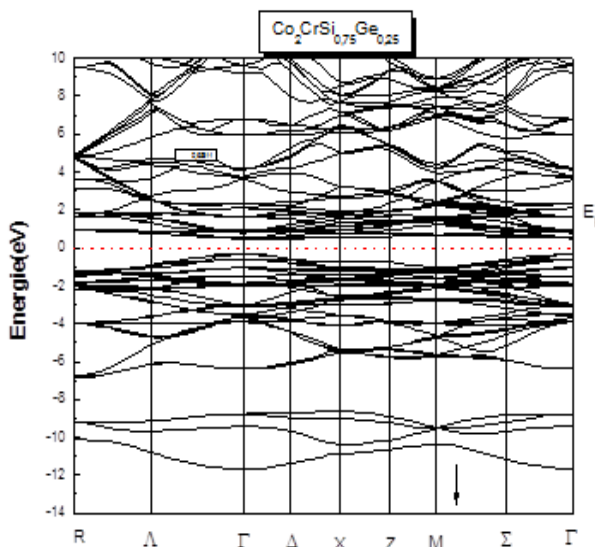
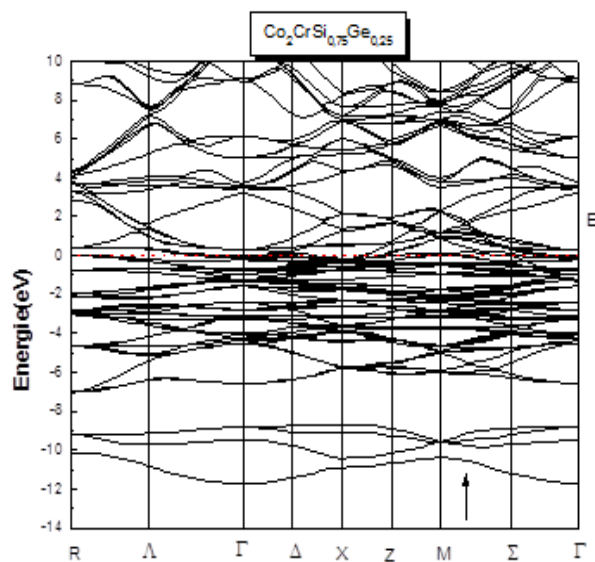
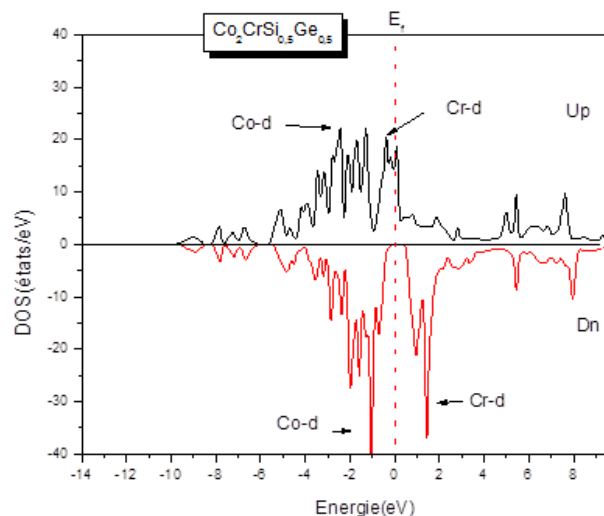
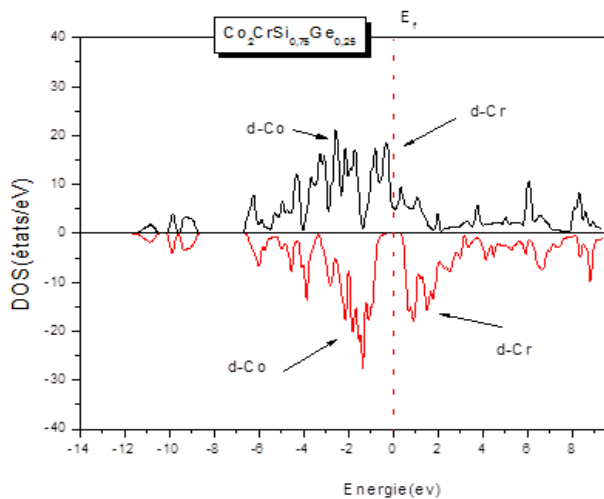


Figure 5. Total and partial density of states of the quaternary Heusler alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$.



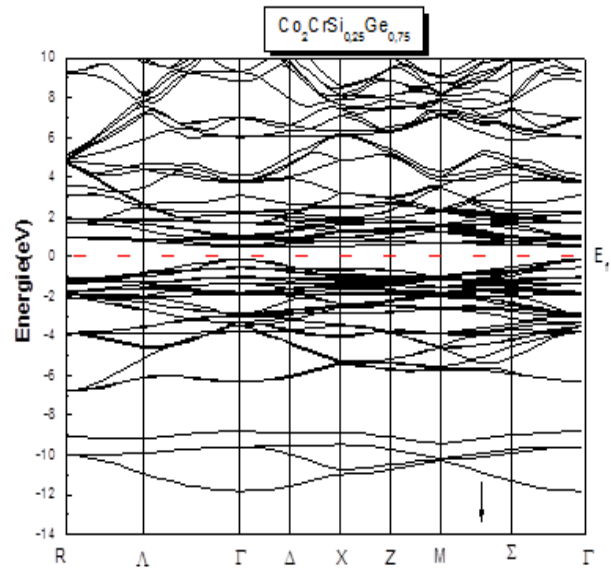
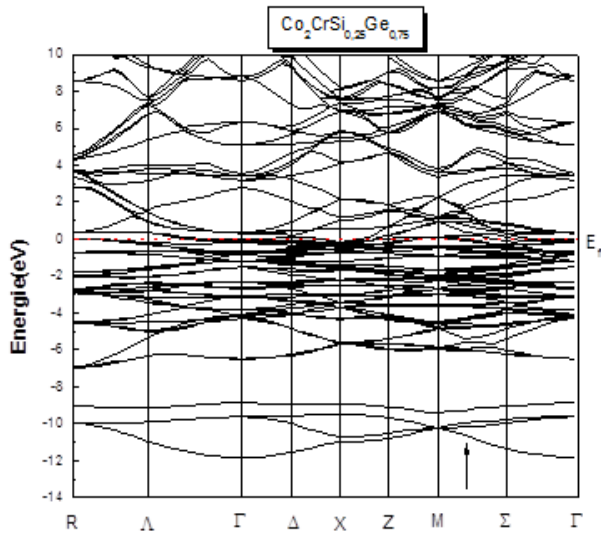
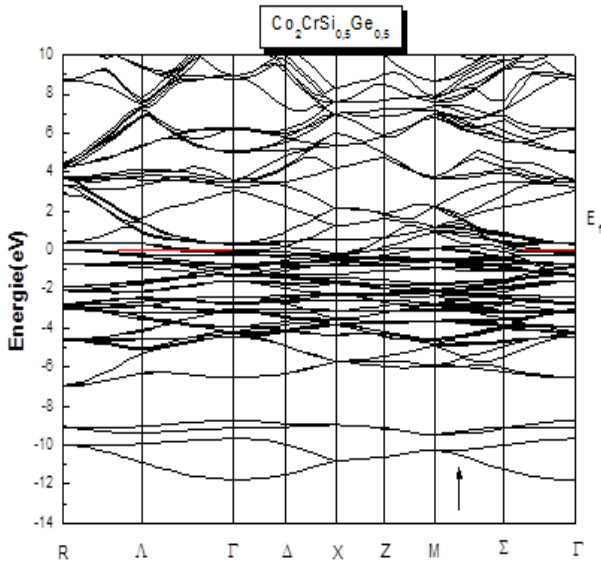


Figure 6. Calculated band structures of the quaternary Heusler alloy $\text{Cr}_2\text{GdSn}_{1-x}\text{Sb}_x$

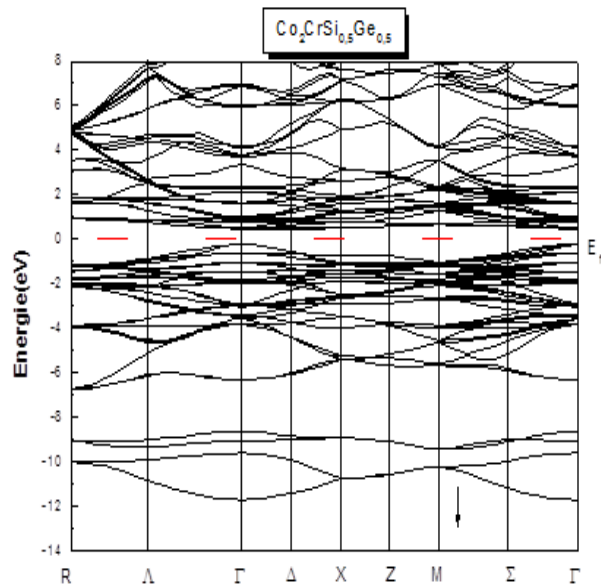


We notice an overlap valence and conduction bands to the state spin-up, while the existence of electronic states at the Fermi level tells us about the nature of these metal alloys. The presence of electronic states is most obvious for the spin up against by it is minimal for the spin down and shows the near character semiconductor. Note that the maximum of the valence band and the minimum of the conduction band are located at the same point X, so this is characteristic of direct gap. It can be said that the compounds and their alloys are semiconductors in the state spin-dn. This means that the system has a half-metallic character. Fig. 6 shows calculated band structures of the quaternary Heusler alloy $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$

The values of the gap energy are summarized in Table 2.

Table 2. Calculated energy gap $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ with concentration x of Ge.

Compound	x	$E_g(\text{eV})$
	0.00	0.8597
	0.25	0.7949
$\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$	0.50	0.6982
	0.75	0.6547
	1.00	0.646



3.4. Magnetic Properties

The magnetic moment per formula unit for the alloys of 3d elements can be determined from the number of their valence electrons using Slater–Pauling (SP) rule [25]. According to this rule, magnetic moment for the half metallic moment for the half metallic full-Heusler alloy is given by $M_t = Z_t - 24$, where M_t is the total magnetic moment per unit cell and Z_t is the total number of valence electrons. The magnetic moment obtained by present calculations is

4.0075 μ_B and 4.0020 μ_B for Co_2CrSi and Co_2CrGe respectively which agrees well with values from Slater–Pauling rule [25] as well as other calculations [26–28]. The energy band structure of a semi-metallic material has an asymmetry between the spin up states and spins down with a gap or a pseudo energy gap at the Fermi level. This gives rise to the polarizations of the conduction electrons at the Fermi level which may reach 100%.

The calculated total and local magnetic moment for constituent elements are given in Table 3.

Table 3. Calculated total and partial magnetic moments (in μ_B) $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$

Magnetic Moment (μ_B)	Compounds		
	$\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$		
	X=0.25	X=0.50	X=0.75
Co	1.0166	0.9953	0.99538
Cr	1.91019	1.93610	1.9549
Si	-0.01562	-0.01984	-0.00630
Ge	-0.00256	-0.00899	-0.0284
Interstitial	0.07672	0.8964	0.08934
Moment Total (μ_B)	4.00152	4.0019	4.0003
Polarisation de spin %	100	100	100

It is evident that the total magnetic moment increases with increasing pressure. The total magnetic moment is constant with increasing composition x . It is important to emphasize that, to our knowledge; the scientific community has no experimental or theoretical value of the magnetic moments in these materials.

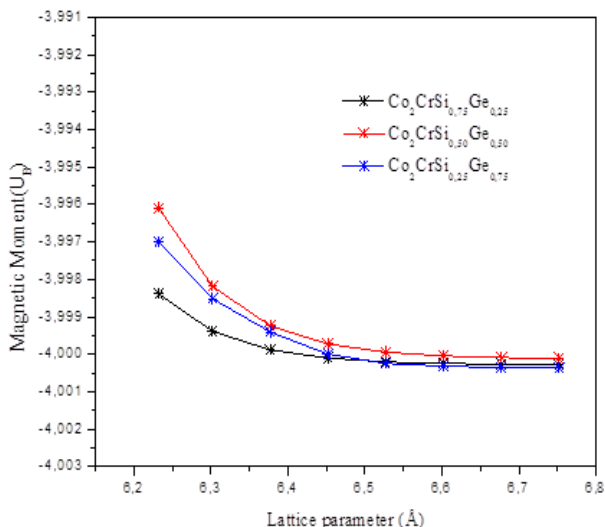


Figure 7. The total magnetic moment as a function of the different lattice parameter for $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ ($x=0.25, 0.50, 0.75$).

3.5. Thermal Properties

We can calculate the thermodynamic quantities for the Heusler alloy $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ through the Debye model

quasi-harmonic implemented in the Gibbs program [29] in which the non-equilibrium Gibbs function $G^*(V, P, T)$.

Through the quasi-harmonic Debye model, one could compute the thermodynamic quantities of any temperatures and pressures of $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ from the calculated $E-V$ data at $T = 0$ and $P = 0$. (T being the temperature and P the pressure).

The relationship between the lattice parameter and the temperature at different pressures is shown in Figure 8 the lattice parameter increases to a very moderate with temperature. On the other hand, it is noted in Figure 9 that the relationship between the bulk modulus and the pressure is virtually linear. The bulk modulus increases with pressure and decreases with temperature.

Further, the temperature effects on the lattice parameters of the quaternary Heusler alloys $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ with the Al concentration 0, 0.25, 0.5, 0.75, 1 are shown in Figure. 13. As expected the volume increases with increasing temperature and the rate of increase is high. In Figure. 14 we report the evolution of the bulk modulus as a function of T at different concentrations. It is worth noting from the regular spacing of the curves observed in Figure.15 that the relationship between the bulk modulus and the temperature is nearly linear at various concentrations ranging from 0 to 1.

The investigation on the heat capacity of crystals is an old topic of the condensed matter physics with which illustrious names are associated. Knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications. Two famous limiting cases are correctly predicted by the standard elastic continuum theory [30]. At high temperatures, the constant-volume heat capacity C_v tends to the Petit and Dulong limit [31], the Figure 10 show the variation of the heat capacity C_v constant volume depending on the temperature for different pressures. This quantity indicates a strong increase up to ~ 500 K, which is due to anharmonic approximation Debye model. Values are purely predictive since we have no experimental data. However, at higher temperatures and at higher pressures, the effect of anharmonic C_v is deleted, and C_v tends towards the limit of Dulong-Petit. ($C_v(T) \cong 74.60\text{J.mol}^{-1}\text{K}^{-1} - 74.46\text{J.mol}^{-1}\text{K}^{-1}$, respectively Co_2CrSi and Co_2CrGe is shown in figure 11.

In figure 11 we present the variation of the Debye temperature θ_D as a function of temperature and pressure, respectively, one can observe that θ_D is nearly constant from 0 to 100K and decreases linearly with increasing temperature from $T > 200$ K. It can be seen that the Debye temperature θ_D increases with pressure and decreases with temperature.

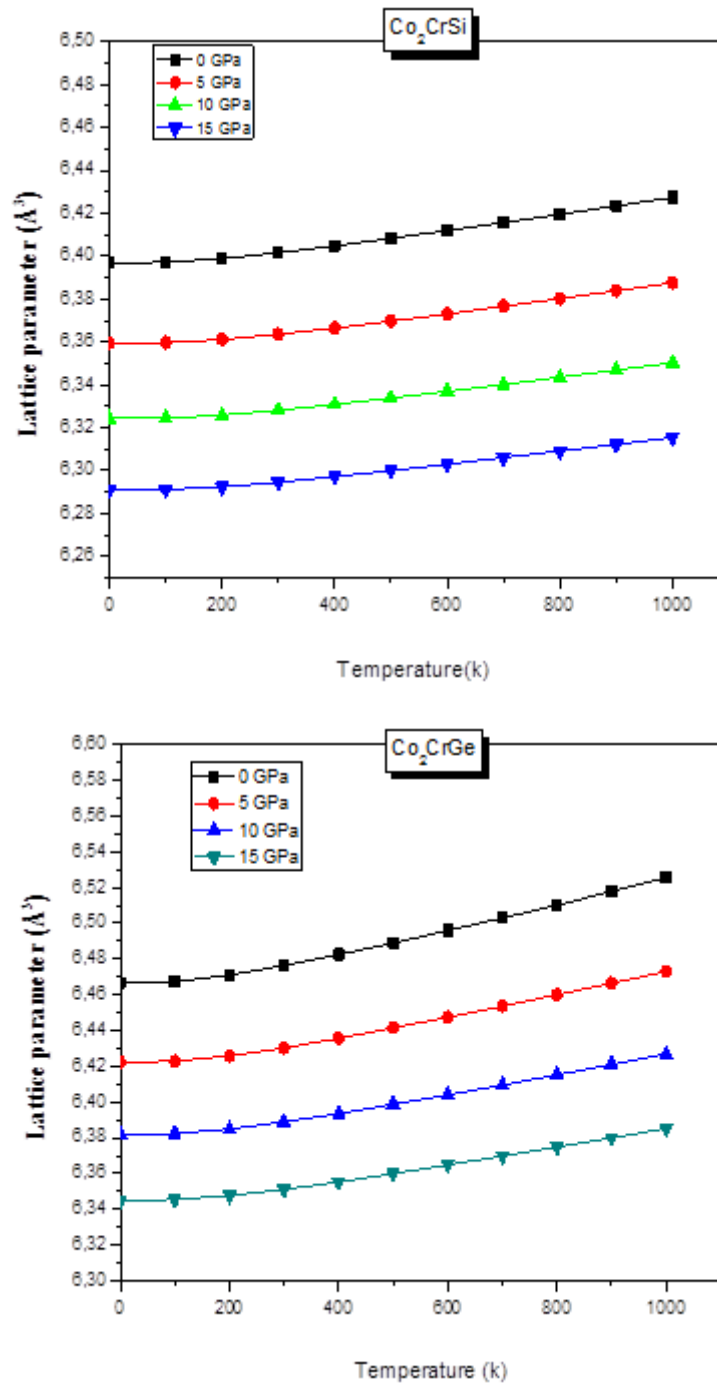


Figure 8. Variation of the lattice parameter as a function of temperature and pressure in Co_2CrSi and Co_2CrGe alloys.

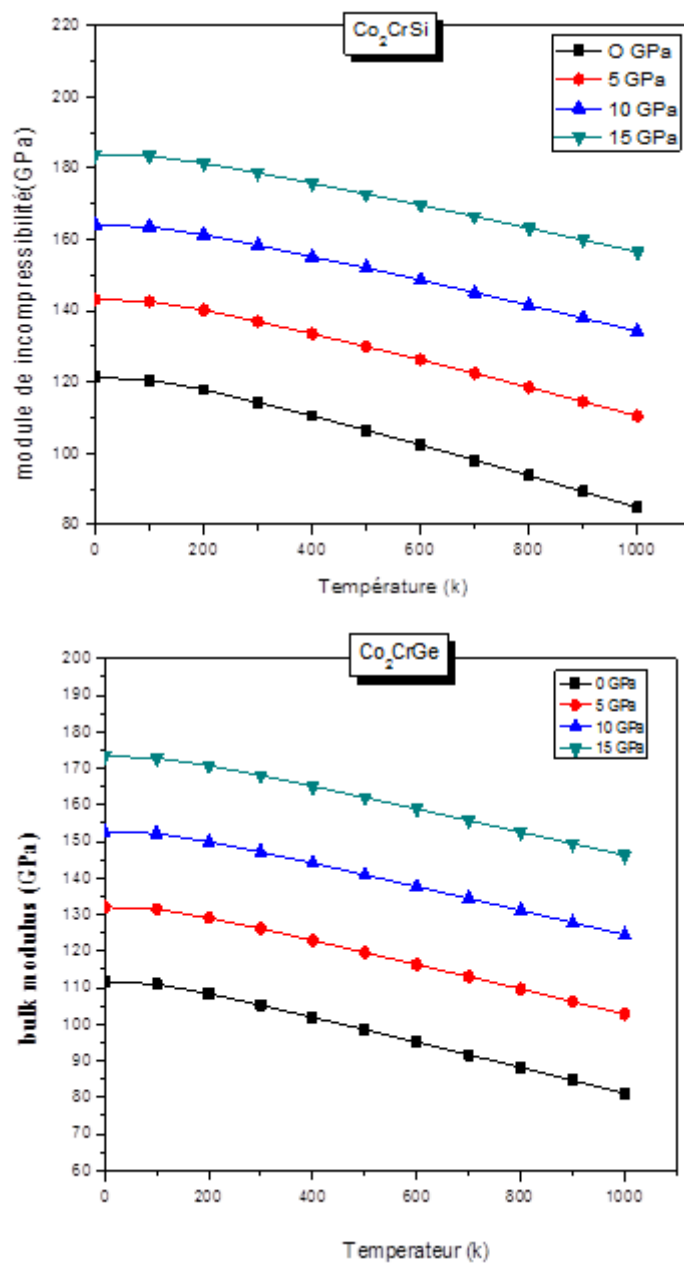


Figure 9. Variation of the bulk modulus as a function of temperature and pressure in Co_2CrSi and Co_2CrGe alloys.

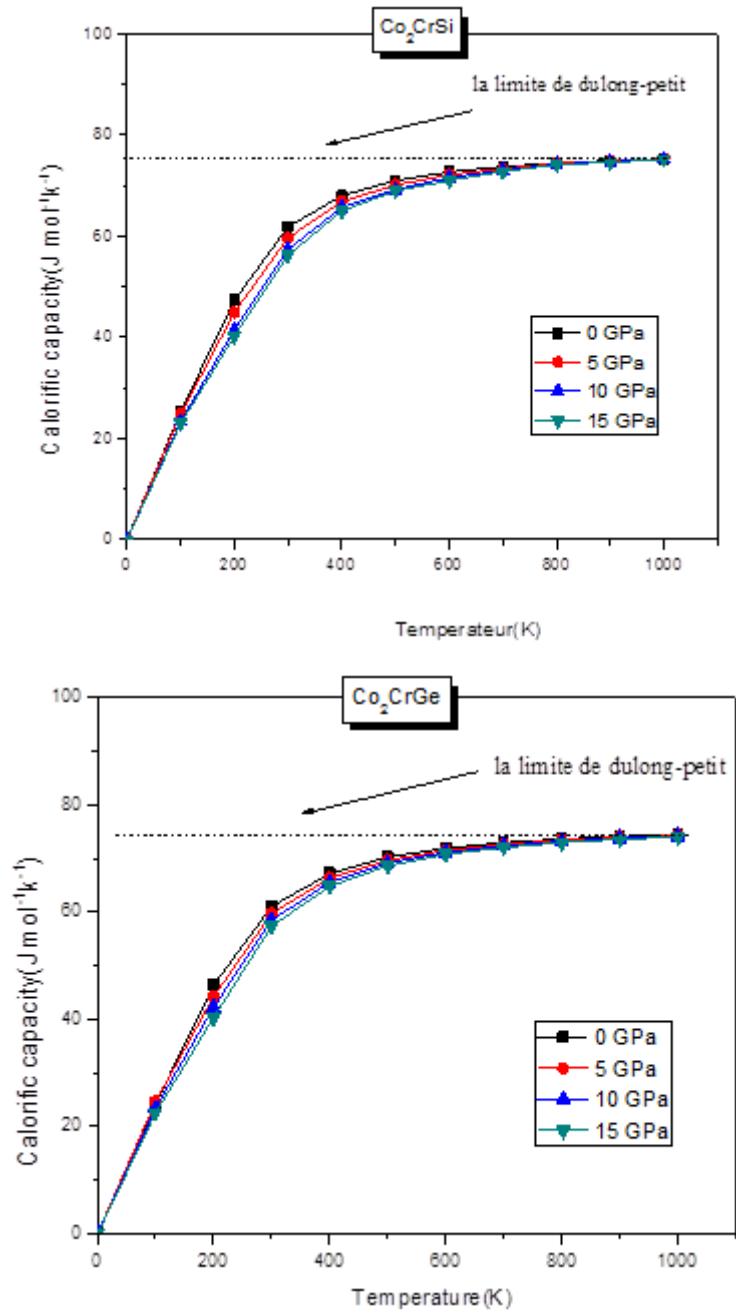


Figure 10. Variation of the heat capacity as a function of temperature and pressure in Co_2CrSi and Co_2CrGe alloys.

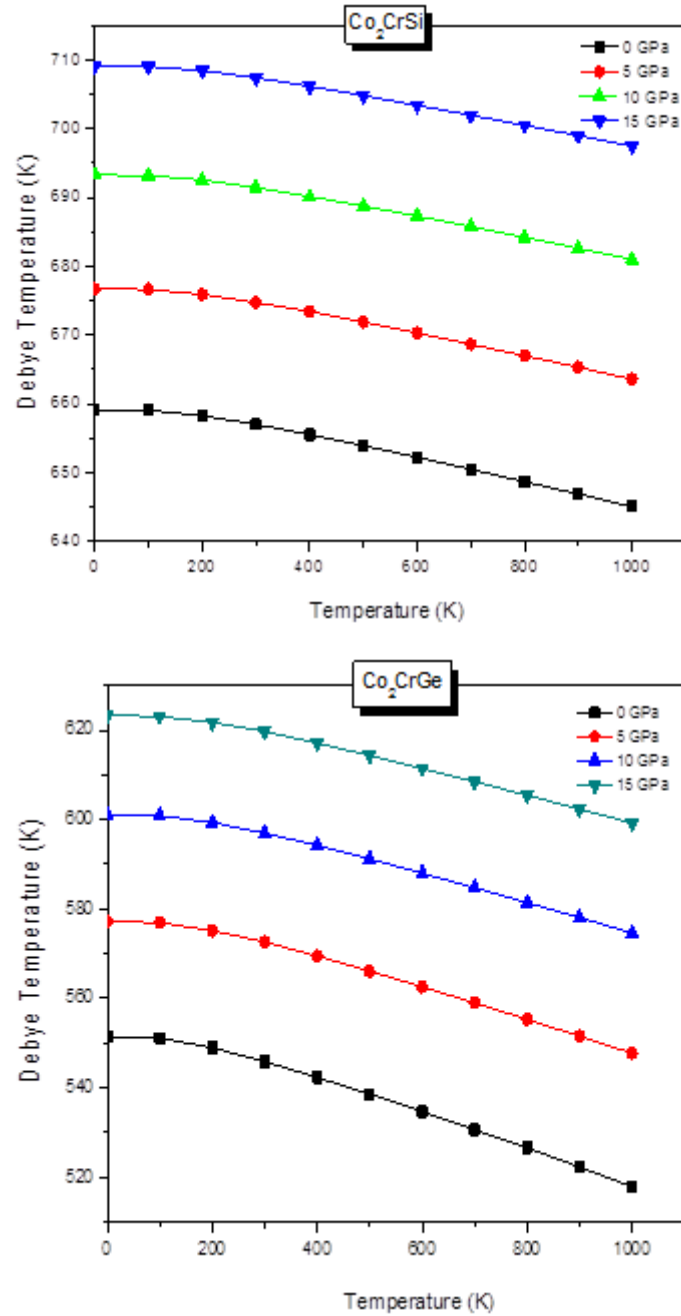


Figure 11. The Debye temperature θ_D as a function of temperature and pressure in Co_2CrSi and Co_2CrGe alloys.

The coefficient of thermal expansion α has been predicted figure.13 He quickly believes in cube power of temperature then tends towards a limit.

We note, for a given pressure α increases with temperature when $T \leq 300\text{K}$ (at low temperature), especially at zero pressure, and tends gradually to increase linearly at higher temperatures. As the pressure increases, the variation of α with the temperature becomes smaller. For a given temperature, α decrease sharply with increasing pressure, and is very low at higher temperatures and higher pressures as well.

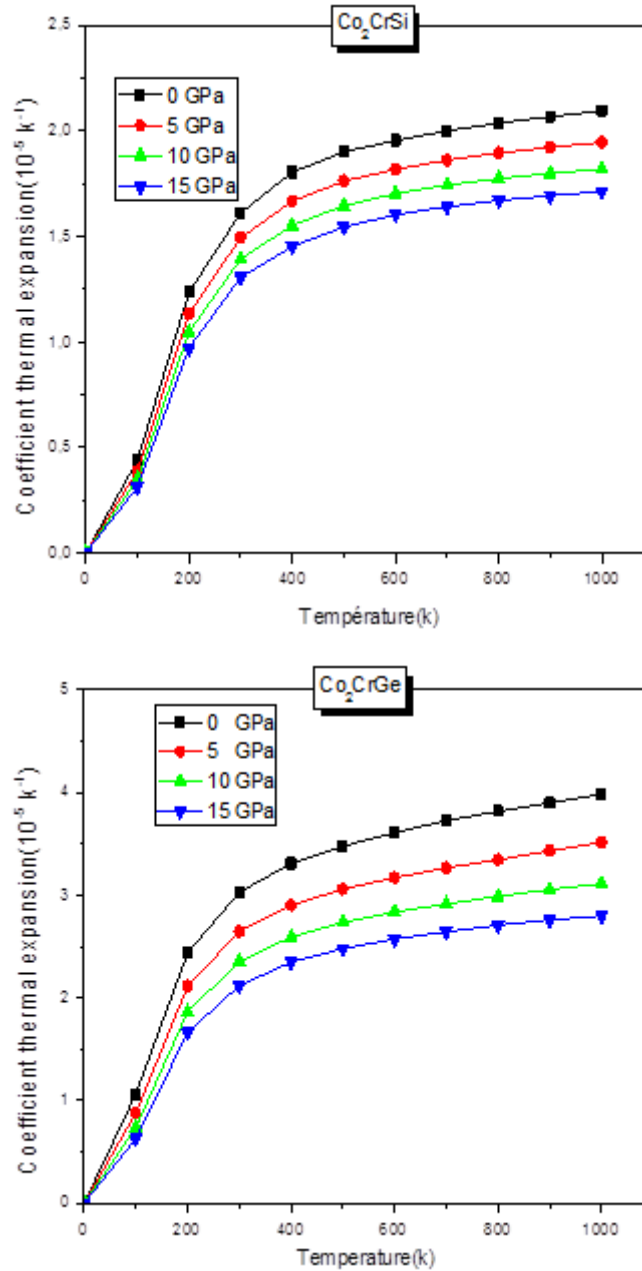


Figure 12. Variation temperature coefficient as a function of temperature for different pressures for Co_2CrSi and Co_2CrGe

The vibrational properties that are related to the thermal effects are the heat capacity CV and the Debye temperature. Our results for the alloys concerning the heat capacity CV at different temperatures depicted in Figure 16. At high temperatures, the heat capacity CV approaches the classical value of $74.60 \text{ J.mol}^{-1}.\text{K}^{-1}$

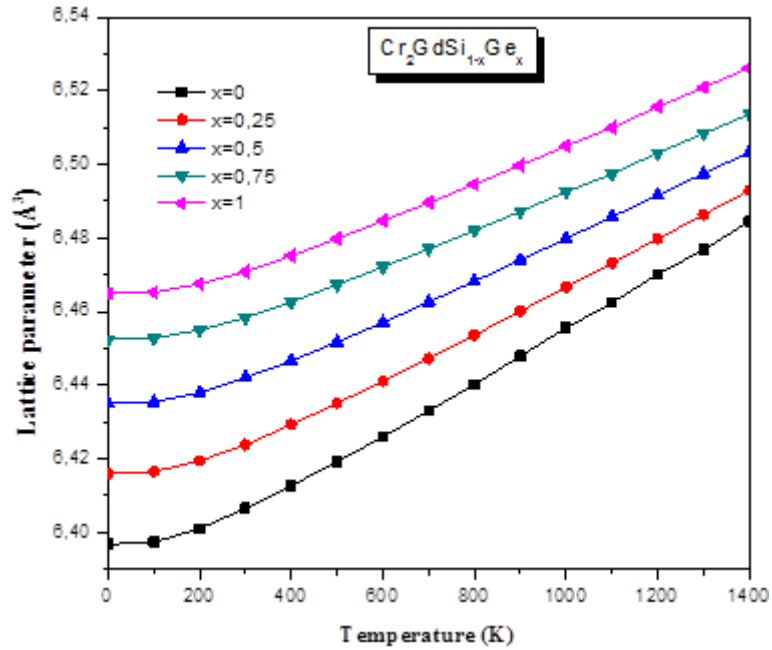


Figure 13. Variation of the lattice parameter as a function of temperature and Al fraction in $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ alloys

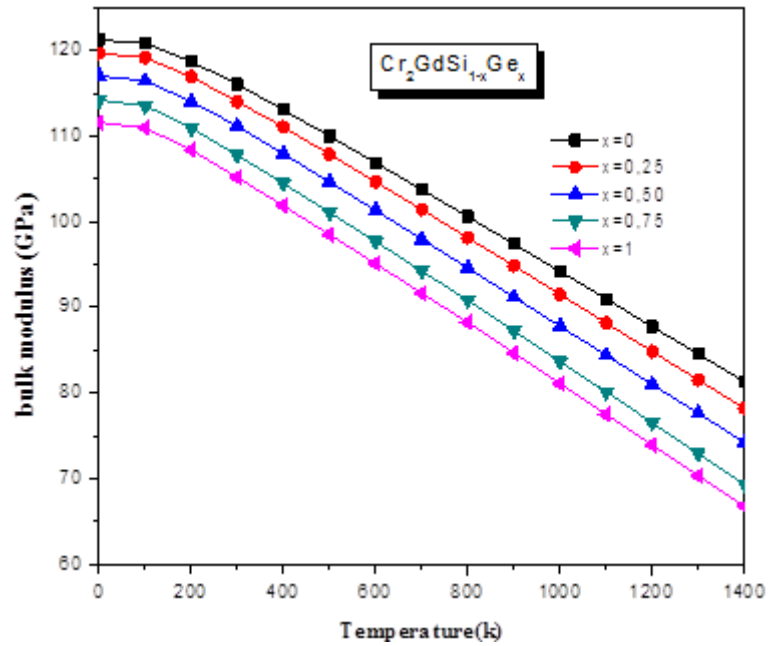


Figure 14. Variation of the bulk modulus as a function of temperature and Al fraction in $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ alloys

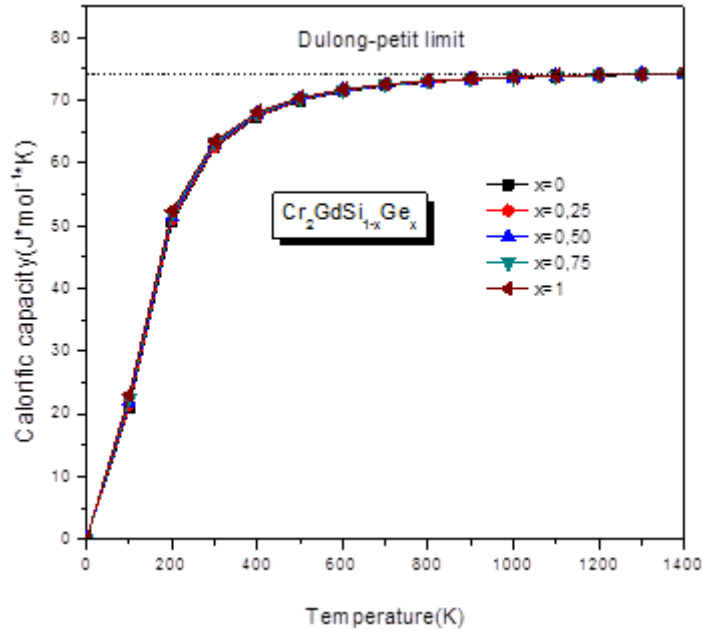


Figure 15. Variation of the heat capacity as a function temperature and Al fraction in $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ alloys

3.6. Thermodynamic Properties

Let us now turn our attention to the phase stability of $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ quaternary Heusler alloys. For this purpose, we calculate the Gibbs free energy of mixing $\Delta G_m(x, T)$, which allows accessing the $T-x$ phase diagram and obtaining the critical temperature T_c . More details of calculations are given in [33–34]. The Gibbs free energy of mixing, for an alloy is expressed as

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Where

$$\Delta H_m = \Omega x(1-x)$$

$$\Delta S_m = -R[x \ln x + (1-x) \ln(1-x)]$$

ΔH_m and ΔS_m are the enthalpy and the entropy of mixing, respectively; Ω is the interaction parameter that depends on the material, R is the ideal gas constant and T is the absolute temperature. The mixing enthalpy of alloys can be obtained as the difference in energy between the alloy and the weighted sum of the constituents:

$$\Delta H_m = E_{ABx} C_{1-x} - xE_{AB} - (1-x)E_{AC}$$

Where $E_{ABx} C_{1-x}$, E_{AB} and E_{AC} are the energies of $\text{AB}_x\text{C}_{1-x}$, AB and AC materials, respectively. We calculate ΔH_m to obtain the interaction parameter Ω as a function of the alloy concentration x . The variation of Ω as a function of the composition x for $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$

quaternary Heusler alloy has been determined in Figure 16. The best fit of our data regarding Ω is found to be linear, yielding the following expression: Ω (kcal mol⁻¹) = 7.547 - 1.624x.

The average value of the x -dependent Ω in the composition range $0 \leq x \leq 1$ is estimated to be 6.737 kcal* mol^{-1} . The larger enthalpy of $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ alloy suggests a large value of Ω and hence a higher critical temperature. Next, in order to determine the stable, metastable and unstable mixing regions of the alloy of interest, we have calculated the temperature–composition phase diagram. Our results are displayed in figure 17. At a temperature lower than the critical temperature T_c , the two binodal points are determined as those points at which the common tangent line touches the ΔG_m curves. Whereas the two spinodal points are determined as those points at which the second derivative of ΔG_m is zero: $\delta^2(\Delta G_m)/\delta x^2 = 0$. A critical temperature (T_c) value of 981.274 K has been evaluated for $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$. The equilibrium solubility limit, i.e. the miscibility gap, is marked by the spinodal curve in the phase diagram. For temperatures and compositions above this curve, a homogeneous alloy is predicted. One can also note the existence of a wide range between spinodal and binodal curves, thus indicating that $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ may have a metastable phase. Hence our results indicate that the alloy $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ is stable at high temperature.

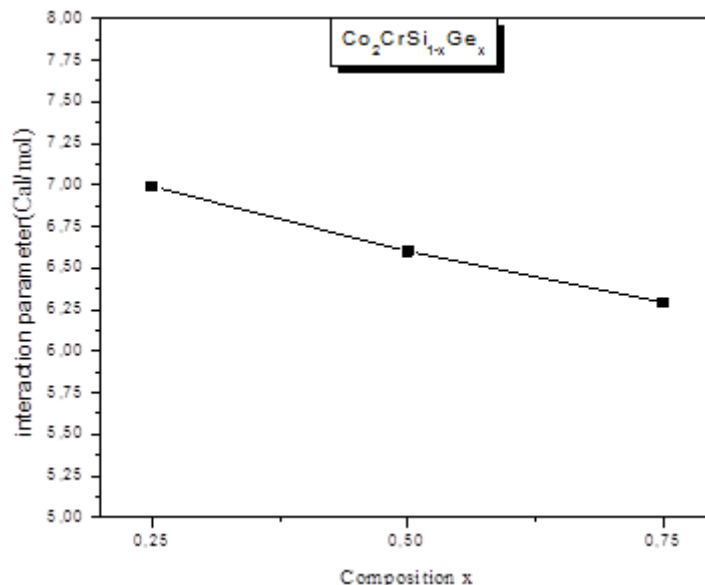


Figure 16. Variation of the interaction parameter of $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ Heusler alloys with Ge Concentration

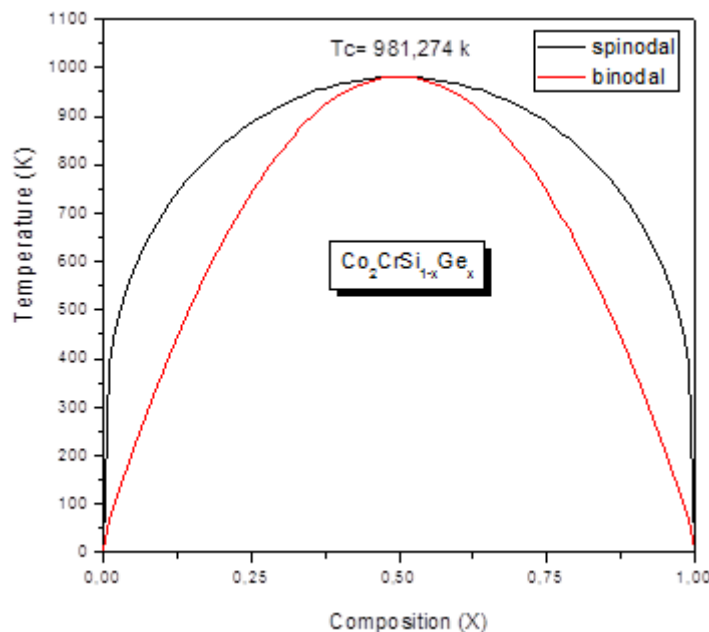


Figure 17. T-x phase diagram for $\text{Co}_2\text{CrSi}_{1-x}\text{Ge}_x$ alloys.

3.7. Enthalpy of Formation

The enthalpy of formation of a crystal ΔH_{form} is defined as the difference between the energy of the crystal and the sum of energies of the constituent elements that crystal in their standard states. To determine the thermodynamic stability and estimate the possibility of synthesizing these alloys, the formation enthalpy can be calculated using the following relationship:

$$\Delta H_{\text{form}}(\text{Co}_2\text{CrZ}) = E_{\text{total}}(\text{Co}_2\text{CrZ}) - [2E_{\text{total}}(\text{Co}_2) + E_{\text{total}}(\text{Cr}) + E_{\text{total}}(\text{Z})]$$

Or $E_{\text{total}}(\text{Co}_2\text{CrZ})$ is the total energy of the compounds present in the L21 Phase.

$E_{\text{total}}(\text{Co}_2)$, $E_{\text{total}}(\text{Cr})$ and $E_{\text{total}}(\text{Z})$ are the calculated total energies atoms in their standard states.

Values training enthalpy for the investigated alloys are shown in Table 4.

We can see that the enthalpy of formation take negative values, for all the compounds studied, calculated from the equation, means the existence and stability and it is possible to synthesize these alloys experimentally.

Table 4. Values of enthalpy of formation ΔH_{form}

Compound	X	$\Delta H_{form}(eV)$
	0.00	-29.2287
	0.25	-27.6563
Co ₂ CrSi _{1-x} Ge _x	0.50	-26.1622
	0.75	-24.8058
	1.00	-23.4974

4. Conclusions

We have investigated in detail the structural, elastic, electronic, magnetic, thermodynamic and thermal properties of the quaternary Heusler alloys Co₂CrSi_{1-x}Ge_x (x = 0, 0.25, 0.5, 0.75, 1) at ambient as well as at elevated temperatures. With the linearized augmented plane wave method based on density functional theory and implemented in WIEN2k code. For exchange correlation potential we have used the generalized gradient approximation (GGA) of Perdew et al. Our interest in this study was justified by the fact that the properties of these compounds are not available in the literature. The choice of compounds was warranted by the great deal of attention given to these Heusler alloys because of their large field of applications. Our calculated structural parameters are reasonable; also C11, C12 and C44 parameters were obtained from calculations. This quaternary Heusler alloy is mechanically stable according to the elastic stability criteria and shows ductile behavior. A linear variation of the lattice constant, elastic constants and Debye temperature with x has been obtained. The calculated lattice parameters for the alloys exhibit a tendency to Vegard's law with a marginal bowing parameter. The electronic band structures show a half-metallic character. The quasi-harmonic Debye model is successfully applied to determine the thermal properties at different temperatures and pressures. The results presented in this paper for the thermodynamic and thermal properties are predictions, and the experiments to prove them are welcomed. Finally, the calculated phase diagram indicated that Co₂CrSi_{1-x}Ge_x is stable at temperature of 981.27 K.

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