Pressure dependent structural, elastic and mechanical properties with ground state electronic and optical properties of half-metallic Heusler compounds Cr$_2$YAl (Y=Mn, Co): first-principles study

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A B S T R A C T
Hydrostatic pressure dependent structural, electronic, elastic and optical properties of Heusler compounds Cr$_2$YAl (Y=Mn, Co) are investigated by the first-principles calculations. Present study shows good agreement between the calculated and experimental values of lattice parameters of these compounds. The gradual decrease of lattice parameter and unit cell volume with the increase of pressure eliminates the possibility of phase transition up to the considered pressure range 0–30 GPa. The absence of negative frequency in the phonon dispersion curves at various external pressures up to 30 GPa confirm the dynamical stability of these compounds. The values of Pugh's ratio, Poisson's ratio and Cauchy pressure indicate the ductility of Cr$_2$CoAl while those criteria confirm the brittleness of Cr$_2$MnAl. Pressure dependent behaviour of the elastic constants of these compounds shows the mechanical stability over the studied pressure range (0–30 GPa). Crystal stiffening of both the compounds is indicated by the increase of Debye temperature with increasing hydrostatic pressure. The pressure dependent band structure and density of states (DOS) calculations reveal the half- and the near half-metallic behaviour of Cr$_2$MnAl and Cr$_2$CoAl, respectively up to 20 GPa while those disappear at pressure around 30 GPa. The variations of optical constants with pressure is consistent with the results of the electronic structure calculations. High reflectivity (>45%) of both the compounds makes them attractive for optoelectronic device applications.

1. Introduction
A class of intermetallic compounds known as Heusler alloys are still attractive in the current century in spite of the fact that these compounds were discovered in 1903 [1]. As there is huge interest of Heusler alloys in various fields especially in spintronics, a lot of them were studied experimentally and theoretically over the last few decades. Many of the Heusler alloys are half metallic; half metallicity indicates that these compounds are metallic for one type of spin and semiconducting for other type of spin. There are scopes to synthesize or predict new Heusler compounds and investigate their various physical properties which can make them suitable for many technological applications, e.g., spintronics [2, 3], magnetic tunnel junction [4], electrodes for giant magnetoresistive spin valves, injection of spins into semiconductors [5], magnonics [6], shape-memory materials [1], spin-torque oscillators [7, 8], magnetic memory [9] etc. Some of these materials can provide an interesting platform for novel quantum phenomena such as quantum Hall effect, quantum chromodynamics etc. [10]. Huesler alloys with superconducting properties also have been reported and attracted significant research interest [11, 12].

Heusler alloys are represented by the generic formula X$_2$YZ (Full Hesulers) and XYZ (Half-Hesulers) both with face-centered cubic (FCC) crystal structure, where X and Y are transition elements and Z is the group III, IV or V elements. For X$_2$YZ Hesuler compounds, X and Y atoms are located at positions (0,0,0), (1/4,1/4,1/4) and (1/2,1/2,1/2); Z atom is located at (3/4,3/4,3/4). There are two types of structures of X$_2$YZ Hesuler compounds: Cu$_2$MnAl-type and Hg$_2$CuTi-type. In Cu$_2$MnAl-type structure, two X atoms are located at the sites (0,0,0) and (1/2,1/2,1/2); Y atom is located at the site (1/4,1/4,1/4); Z atom is located at the site (3/4,3/4,3/4). On the other hand, in Hg$_2$CuTi-type structure, two X atoms are located at the sites (0,0,0) and (1/4,1/4,1/4); Y atom is located at the site (1/2,1/2,1/2); Z atom is located at the site (3/4,3/4,3/4) [13].

Jamer et al prepared bulk Cr$_2$CoAl and predicted the presence of both ferrimagnetic and paramagnetic phases [14]. Under Argon atmosphere,
polycrystalline Cr$_2$CoAl was synthesized by arc melting [15]. When the alloy Cr$_2$CoAl was cooled below 28K, the compound would be ferromagnetic. A study of effect of disorder in Cr$_2$CoAl shows that spin magnetic moment varies with atomic disorder [16]. Ab initio calculations of structural stability, magnetism, and electronic structure of Cr$_2$MnAl, Cr$_2$CoAl and some other Heusler compounds are done by various research groups [5, 14, 17, 18, 19]. There is a density functional theory (DFT) study regarding undoped and Fe-doped Cr$_2$CoAl [20]. This study predicted that these compounds are not true half-metallic ferromagnets. Another computational study showed that Cr$_2$CoAl is a compensated half-metal (CHM) [21]. There is a DFT study which confirms the half metallicity of Cr$_2$MnAl [22]. According to this study, the magnetic moment calculation of Cr$_2$MnAl is consistent with Slater-Pauling rule.

Study of optical properties can provide useful insight which is helpful to judge the adaptability of potential application in optoelectronic device construction. One recent computational study focused only on the ground state optical properties of Cr$_2$CoAl [19]. To the best of our knowledge, optical properties of Cr$_2$MnAl are not yet explored. Here we focus on the ground state as well as the pressure dependent optical properties of these compounds. The effect of pressure on lattice parameter, unit cell volume and the elastic properties are important because it can identify any structural phase change and unstable condition of the compounds. Pressure dependence of the structural, elastic and mechanical properties of the compounds Cr$_2$YAl (Y=Mn, Co) are studied here. The phonon dispersion curve usually helps to understand the dynamical stability of solids. The absence of imaginary frequency in dispersion curves suggests the stability of a system. The phonon dispersion curves of Cr$_2$MnAl and Cr$_2$CoAl along high symmetry directions in the Brillouin zone up to pressure 30 GPa are investigated. The Debye temperature and the acoustic velocities are also calculated because these parameters along with elastic constants are important to find their potential industrial applications. The study of the electronic properties such as band structure and DOS helps to judge the conducting nature and to explain the optical properties of a compound. Thus the effect of pressure on the ground state band structure and DOS of these compounds are also studied.

2. Computational method

DFT is a quantum theory based popular method to calculate physical properties of a solid system. Computational study of Cr$_2$YAl (Y=Mn, Co) are done by Cambridge Serial Total Energy Package (CASTEP) code [23] based on DFT [24, 25]. To evaluate exchange correlation energy PBE-GGA scheme is used [26]. The electron-ion interaction is considered by Vanderbilt type ultrasoft pseudopotentials [27]. Broyden, Fletcher, Goldfrab and Shanno technique is used to optimize the structure [28]. To optimize the crystal structure and to calculate all the properties including DOS of Cr$_2$CoAl (Cr$_2$MnAl) a plane wave cut off energy of 500 eV (350 eV) and $12 \times 12 \times 12 (9 \times 9 \times 9)$ Monkhorst-Pack grid [29] are used. Convergence threshold for total energy is taken as $1 \times 10^{-5}$ eV/atom. The calculations are done with the convergence threshold of 0.03 eV/A for the maximum force, 0.05 GPa for maximum stress, and 0.001A for maximum displacement. The phonon dispersion calculations are performed by using the finite displacement supercell method [30] considering a $3 \times 3 \times 3$ supercell, cut off energy of 310 eV and $k$ point mesh of $7 \times 7 \times 7$.

3. Results and discussion

3.1. Structural properties

Both Cr$_2$YAl (Y=Mn, Co) possess a unit cell having FCC structure with space group $F\bar{4}3m$ (No.216). The unit cell having four formula units contains 16 atoms. The crystal structure of Cr$_2$YAl (Y=Mn, Co) is shown in Figure 1. In the unit cell of Cr$_2$YAl (Y=Mn, Co), Cr atom occupies the Wyckoff positions (0,0,0) and (1/4,1/4,1/4), Y and Al atoms occupy the Wyckoff positions (1/2,1/2,1/2) and (3/4,3/4,3/4), respectively. Table 1 lists the calculated lattice constant, unit cell volume and bulk modulus of Cr$_2$MnAl and Cr$_2$CoAl at external pressures from 0 to 30 GPa at an interval of 5 GPa along with previously available experimental and computational data for comparison. For Cr$_2$CoAl, the deviations of calculated lattice constant at 0 GPa from the experimental data are 0.98% [14] and 0.38% [15], unfortunately there is no available lattice constant data for Cr$_2$MnAl to compare.

Other parameters presented in Table 1 show good agreement with the previous reports. Hence these first principles calculations are considered to be reliable. It is evident from Table 1 that the pressure dependent values of lattice constants and unit cell volumes of Cr$_2$YAl (Y=Mn, Co) decrease gradually with hydrostatic pressure. This implies the structural stability of both the compounds over the studied pressure range (0–30 GPa). Moreover, the phonon dispersion curve helps to examine the dynamical stability of compounds. Figure 2(a)-(h) displays the calculated phonon dispersion curves of Cr$_2$MnAl and Cr$_2$CoAl along the high symmetry directions $W-L-F-X-W-K$ in the Brillouin zone at external pressures from 0 to 30 GPa at an interval of 10 GPa. The absence of any imaginary phonon frequency in the phonon dispersion curves of Cr$_2$MnAl and Cr$_2$CoAl at different external pressures indicates their dynamical stability over the studied pressure range.

3.2. Elastic properties

The crystal structure of a material has great influence on the elastic properties which give a relation between its mechanical and dynamical behaviour. DFT calculations are done to study the elastic properties of the Heusler compounds Cr$_2$YAl (Y=Mn, Co). The calculations are done within Generalized Gradient Approximation. The finite strain theory is applied to calculate the elastic constants of Cr$_2$YAl (Y=Mn, Co) [31, 32].
constant from the calculated values of single crystal elastic constants. The elastic stability criteria [34]:

\[ C'' = C_{12} - C_{44} \]  
\[ \zeta = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \]  

Due to symmetry of cubic structure, the number of independent single crystal elastic constants reduces to three from twenty-one. As both Cr$_2$MnAl and Cr$_2$CoAl possess cubic structure, they have three independent elastic constants: $C_{11}$, $C_{12}$ and $C_{44}$. Table 2 shows the calculated values of elastic constants $C_{11}$, $C_{12}$, $C_{44}$, Cauchy pressure ($C''$) and Kleinman parameter ($\zeta$) of Cr$_2$YAl (Y=Mn, Co) at external pressures from 0 to 30 GPa at an interval of 5 GPa. There is a good agreement between these data with available theoretical studies at 0 GPa. $C''$ and $\zeta$ are calculated from the formulas mentioned below:

\[ C'' = C_{12} - C_{44} \]  
\[ \zeta = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \]  

In order to be regarded as mechanically stable compound, Cr$_2$MnAl and Cr$_2$CoAl have to satisfy the stability criteria for cubic crystal [33]:

\[ C_{11} + 2C_{12} > 0, \]
\[ C_{44} > 0, \]
\[ C_{11} - C_{12} > 0 \]

Mechanical stability of the compounds Cr$_2$YAl (Y=Mn, Co) is confirmed from the calculated values of elastic constants $C_{11}$, $C_{12}$, $C_{44}$. At pressure $P$, the cubic structure has to satisfy the following the mechanical stability criteria [34]:

\[ (C_{11} + 2C_{12}) / 3 + P/3 > 0, \]
\[ C_{44} - P > 0, \]
\[ (C_{11} - C_{12}) / 2 - P > 0 \]

Hence the mechanical stability of both Cr$_2$MnAl and Cr$_2$CoAl is not interrupted in the studied pressure range (0–30 GPa) which indicates the difficulty in unidirectional deformation compared to the shear deformation. The unidirectional compression along the crystallographic direction increases with hydrostatic pressure over the studied pressure range. For both Cr$_2$CoAl and Cr$_2$MnAl, the value of $C_{44}$ also increases with pressure up to 30 GPa which indicates the increasing response of the compounds to shear deformation.

The variations of single crystal elastic constants ($C_{11}$, $C_{12}$, $C_{44}$) with pressure are presented by bar graphs in Figure 3(a)-(c) at external pressures from 0 to 30 GPa at an interval of 5 GPa.

Table 1. Calculated lattice parameters $a$ (Å), unit cell volume $V$ (Å$^3$) and bulk modulus $B$ (GPa) for Cr$_2$CoAl and Cr$_2$MnAl up to pressure ($P$) 30 GPa.

| Compound | P (GPa) | $a$ (Å) | $V$ (Å$^3$) | $B$ (GPa) | Deviation of lattice constant (%) | Method | Reference |
|----------|---------|---------|-------------|-----------|----------------------------------|--------|-----------|
| Cr$_2$CoAl | 0       | 5.794   |             | 0.98      | Expt. [14]                        |        |           |
|          | 0       | 5.760   |             | 0.38      | Expt. [15]                        |        |           |
|          | 0       | 5.770   |             | 0.55      | GGA [20]                          |        |           |
|          | 0       | 5.738   | 188.958     | 228.21    | GGA This work                     |        |           |
|          | 5       | 5.69    | 184.220     | 230.18    |                                  |        |           |
|          | 10      | 5.66    | 181.321     | 257.97    |                                  |        |           |
|          | 15      | 5.62    | 177.504     | 290.71    |                                  |        |           |
|          | 20      | 5.59    | 174.677     | 307.98    |                                  |        |           |
|          | 25      | 5.56    | 171.880     | 313.73    |                                  |        |           |
|          | 30      | 5.53    | 169.112     | 331.98    |                                  |        |           |
| Cr$_2$MnAl | 0       | 5.831   |             | 0.99      | GGA [5]                           |        |           |
|          | 0       | 5.850   |             | 0.67      | GGA [17]                          |        |           |
|          | 0       | 5.866   |             | 141.83    | GGA [22]                          |        |           |
|          | 0       | 5.889   | 204.23      | 125.29    | GGA This work                     |        |           |
|          | 5       | 5.82    | 197.137     | 159.67    |                                  |        |           |
|          | 10      | 5.77    | 192.100     | 186.68    |                                  |        |           |
|          | 15      | 5.72    | 187.149     | 214.44    |                                  |        |           |
|          | 20      | 5.68    | 183.250     | 236.23    |                                  |        |           |
|          | 25      | 5.64    | 179.406     | 258.07    |                                  |        |           |
|          | 30      | 5.60    | 175.616     | 274.55    |                                  |        |           |

The elastic modulus suggested by Hill is the average of the moduli suggested by Voigt and Reuss [35]. Strain distribution is assumed to be
continuous in Voigt approximation, while Reuss assumes discontinuity in strain distribution [36]. On the other hand, stress distribution is approximated to be discontinuous in Voigt approximation and continuous in Reuss approximation. For both the compounds Cr$_2$MnAl and Cr$_2$CoAl, the lower value of $G$ (87.62 and 96.25 GPa for Cr$_2$MnAl and Cr$_2$CoAl, respectively) as compared to that of $B$ (125.29 and 228.21 GPa for Cr$_2$MnAl and Cr$_2$CoAl, respectively) indicates the dominance to the failure of the materials through shear deformation. Young’s modulus measures the stiffness against longitudinal deformation [37, 38]. It is also a significant parameter to measure thermal shock resistance of a

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**Figure 2.** Phonon dispersion curves of the considered compounds along the high symmetry directions W-L-F-X-W-K. Calculated phonon dispersion of Cr$_2$MnAl at pressures (a) 0 GPa, (b) 10 GPa, (c) 20 GPa and (d) 30 GPa. Calculated phonon dispersion of Cr$_2$CoAl at (e) 0 GPa, (f) 10 GPa, (g) 20 GPa and (h) 30 GPa.
material. The larger the value of Young's modulus, the smaller the thermal shock resistance. Thermal shock resistance of Cr$_2$MnAl is larger than that of Cr$_2$CoAl.

The variations of B, G and Y with pressure are also presented by bar graphs in Figure 3(d)–(f) at external pressures from 0 to 30 GPa at an interval of 5 GPa. It is evident from Table 2, Table 3 and Figure 3(a)–(f)

Table 2. Calculated elastic constants $C_p$ (GPa), Cauchy pressure $C^0$ (GPa) and Kleinman parameter $\zeta$ of Cr$_2$YAl (Y=Mn, Co) up to pressure ($P$) 30 GPa.

| Compound | $P$ (GPa) | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{44}$ (GPa) | $C^0$ (GPa) | $\zeta$ | Reference |
|----------|-----------|----------------|----------------|----------------|-------------|--------|-----------|
| Cr$_2$CoAl | 0 | 345.29 | 169.68 | 103.58 | 66.110 | 0.618 | This work |
| | 5 | 355.37 | 167.59 | 104.92 | 62.670 | 0.601 | |
| | 10 | 390.95 | 191.47 | 112.83 | 78.640 | 0.616 | |
| | 15 | 431.33 | 220.39 | 120.55 | 99.840 | 0.634 | |
| | 20 | 455.86 | 234.05 | 127.91 | 106.140 | 0.636 | |
| | 25 | 468.69 | 236.25 | 134.66 | 101.590 | 0.628 | |
| | 30 | 493.73 | 251.11 | 141.27 | 109.840 | 0.632 | |
| Cr$_2$MnAl | 0 | 246 | 89.70 | 104.60 | 0.503 | This work |
| | 0 | 218.39 | 78.74 | 101.99 | -23.250 | 0.503 | [22] |
| | 5 | 263.85 | 107.58 | 117.30 | -9.720 | 0.545 | |
| | 10 | 299.69 | 130.17 | 129.51 | 0.660 | 0.569 | |
| | 15 | 336.12 | 153.60 | 140.01 | 13.590 | 0.588 | |
| | 20 | 365.19 | 171.74 | 149.11 | 22.630 | 0.600 | |
| | 25 | 393.28 | 190.46 | 157.25 | 33.210 | 0.612 | |
| | 30 | 415.6 | 204.04 | 164.34 | 39.700 | 0.617 | |

Figure 3. Pressure dependence of elastic constants (a) $C_{11}$, (b) $C_{12}$, (c) $C_{44}$, (d) B, (e) G, (f) Y of Cr$_2$YAl (Y=Mn, Co) from 0 to 30 GPa at an interval of 5 GPa.
that $C_{11}$, $C_{12}$, $C_{44}$ and $B$, $G$, $Y$ increase gradually with pressure for both Cr$_2$MnAl and Cr$_2$CoAl suggesting that these compounds are mechanically stable over the studied pressure range.

Ductility and brittleness of a compound is determined by various parameters such as Pugh's ratio [39], Poisson's ratio [40] and Cauchy pressure [41]. The ductility and brittleness limits are as follows: 0.5 is the limit for Pugh's ratio ($G/B$), 0.31 is the limit for Poisson's ratio and positive value of Cauchy pressure is the indicator of ductility. A compound having Pugh's ratio less than 0.5 is regarded as a ductile one. Hence Cr$_2$CoAl is ductile but Cr$_2$MnAl is brittle in nature which is evident from the values of Pugh's ratio shown in Table 3. The value of Poisson's ratio $\nu$ has to be larger than 0.31 for a ductile material. So that Cr$_2$CoAl is ductile while Cr$_2$MnAl is brittle according to this criterion. The value of Cauchy pressure is positive for the compound Cr$_2$CoAl which indicates the ductile nature of this compound. On the other hand, negative value of Cauchy pressure points out the brittleness of Cr$_2$MnAl.

The value of Poisson's ratio $\nu$ also indicates the type of bonding in a compound. The values of $\nu$ are 0.10, 0.25 and 0.33 which correspond to the dominance of covalent, ionic and metallic bonding, respectively. The value of $\nu$ is 0.314 for Cr$_2$CoAl which indicates the dominant metallic nature. On the other hand, $\nu = 0.216$ corresponds to the mixture of covalent and ionic bonding in Cr$_2$MnAl having slight dominance of ionic contribution. The covalent nature of Cr$_2$MnAl vanishes with increasing pressure while metallic contribution is evident for Cr$_2$CoAl over the entire pressure range.

Kleinman parameter $\zeta$ [42] indicates the type of bonding in a compound. The contribution of bond bending or bond stretching to withstand the external pressure is determined by the value of $\zeta$. The value of $\zeta = 0$ corresponds to the dominance of bond stretching while $\zeta = 1$ corresponds to the dominance of bond bending. Strength of Cr$_2$CoAl is dominated by bond bending which is evident from the value of $\zeta$ [cf. Table 2]. On the other hand, almost equal contribution of bond bending and bond stretching to the strength of Cr$_2$MnAl is expected from the value of $\zeta$. $\zeta$ is pressure dependent. A gradual increase of this parameter with hydrostatic pressure is observed for Cr$_2$MnAl while anomalous behaviour is observed for Cr$_2$CoAl [cf. Table 2]. This implies that bond bending contribution to the strength of Cr$_2$MnAl increases progressively with pressure.

Machinability index $\mu$ is used to judge the industrial applicability of a compound. A material is regarded as good in cutting if its machinability index is large. The values of $\mu$ for Cr$_2$MnAl and Cr$_2$CoAl are 1.228 and 2.203, respectively. This indicates that Cr$_2$CoAl is more machinable than Cr$_2$MnAl. A smooth increase in machinability with pressure is observed for Cr$_2$MnAl while the behaviour of Cr$_2$CoAl in terms of machinability is abrupt over the studied pressure range.

Vickers Hardness of the compounds Cr$_2$MnAl and Cr$_2$CoAl [43, 44] is calculated by using formula (7). The hardness values presented in Table 3 indicates that Cr$_2$MnAl is harder than Cr$_2$CoAl. This implies that Cr$_2$MnAl resists more plastic deformation as compared to Cr$_2$CoAl. It is also observed that both the compounds become harder with increasing pressure over the studied range.

### 3.3. Debye temperature and ultrasonic properties

Table 4 presents the calculated values of density $\rho$, Debye temperature $\theta_D$, longitudinal sound velocity $v_l$, shear sound velocity $v_t$ and average sound velocity $v_m$ for the Heusler alloys Cr$_2$MnAl and Cr$_2$CoAl.

Debye temperature is a very important parameter which is used to interpret various properties such as thermal conductivity, melting temperature etc. Average sound velocity $v_m$ which is required to determine Debye temperature can be calculated from the values of elastic constants. The formulas which are used to calculate Debye temperature $\theta_D$, longitudinal sound velocity $v_l$, shear sound velocity $v_t$ and average sound velocity $v_m$ are as follows [45]:

$$\theta_D = \frac{h}{k_B} \left( \frac{3n}{4\pi} \left( \frac{n N_A}{M} \right) \right)^{1/3} v_m$$  \hspace{1cm} (10)

$$v_m = \left[ \frac{\pi}{3} \left( \frac{2}{v_l^2} + \frac{1}{v_t^2} \right) \right]^{1/3}$$  \hspace{1cm} (11)

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}}$$  \hspace{1cm} (12)

$$v_t = \sqrt{\frac{G}{\rho}}$$  \hspace{1cm} (13)

where $h$ is Planck’s constant is, $k_B$ Boltzmann’s constant, $n$ is the number of atoms in the molecule, $\rho$ is the density, $N_A$ is the Avogadro number and $M$ is the molecular weight.

Hardness of a compound is related to the Debye temperature. The higher the Debye temperature, the harder the compound. The values of Debye temperature are 848.2 K and 901.29 K for Cr$_2$MnAl and Cr$_2$CoAl,
respectively [cf. Table 4]. Hence large value of Debye temperature corresponds to high degree of hardness of the Heusler alloys Cr$_2$MnAl and Cr$_2$CoAl. The increase of the Debye temperature with increase of hydrostatic pressure indicates the crystal stiffening of both the compounds.

### 3.4. Electronic properties

Band structure, total and partial density of state calculations is important to study electronic properties of the compounds Cr$_2$MnAl and Cr$_2$CoAl. Optical properties of a compound are directly related to the band structure of the compound. Electronic band structure is calculated at zero pressure along the high symmetry directions $W$-$L$-$I'$-$X$-$W'$-$K$ in the first Brillouin zone. Figure 4(a)-(d) and 4(e)-(h) show the band structures of Cr$_2$CoAl at external pressures from 0 to 30 GPa at an interval of 10 GPa for spin-up and spin-down channels, respectively. The Fermi level ($E_F$) is represented by the horizontal dashed line. The calculated band structures of Cr$_2$CoAl for spin-up and spin-down channels are consistent with the previous computational study [21]. It is evident from the band diagram, Figure 4(a) that there is a band gap near $E_F$, suggesting the non-metallic nature of Cr$_2$CoAl for spin-up channel.

On the other hand, the band structure with no band gap as shown in Figure 4(e) indicates the metallic nature of Cr$_2$CoAl for spin-down channel. This happens because of the crossing of bands at $E_F$. Hence band structure of the Heusler compound Cr$_2$CoAl confirms the near half metallicity of this compound. It is relevant to mention that a compound is regarded as near half-metal if a band gap is observed outside the Fermi level in the band structure for one of the spin channels or the DOS at $E_F$ is very small [5]. The band gap of Cr$_2$CoAl for up spin channel is found 0.13 eV at 0 GPa and increases with the increase of pressure up to 20 GPa Figure 4(a)-(d). Above 20 GPa the band gap reduces to zero. On the other hand, the metallic nature of Cr$_2$CoAl for down spin channel retain up to pressure 30 GPa [Figure 4(e)-(h)]. So the near half-metallic character of Cr$_2$CoAl seems to be suppressed by external pressure at around 30 GPa and therefore the compound becomes metallic.

In order to interpret the contributions of individual atoms to the total density of states (TDOS), the partial density of states (PDOS) for the atoms constituting the structure are calculated. Figure 5(a) represents the TDOS and PDOS of the compound Cr$_2$CoAl for both up and down-spin channels. The Fermi level is represented by the vertical dotted line (red colour) at 0 eV. PDOS of Cr, Co, Al are calculated to describe the contribution of these atoms to the TDOS of Cr$_2$CoAl. Firstly, TDOS and PDOS of Cr$_2$CoAl for the up spin are described in which positive value of DOS is for spin-up electrons. At the $E_F$, value of TDOS is negligible, which indicates non-metallic behaviour of the compound Cr$_2$CoAl for up-spin channel. It is noticeable that there is no contribution from the orbitals of Al to the TDOS. Here, contribution of Co 3d state to the TDOS below the $E_F$ is significant along with the contribution from Cr 3d state. Another remarkable feature of the TDOS curve is the presence of a peak above the $E_F$ at 2 eV which arises mainly due to Cr 3d orbital.

On the other hand, negative value of DOS is for spin-down electrons in the TDOS and PDOS curves. At $E_F$, high value of TDOS is evident which confirms the metallic nature of Cr$_2$CoAl for spin down channel. The contributions to the TDOS at $E_F$ originate from Cr 3d and Co 3d states. It is noticeable that there is no contribution from the orbital of Al atom to the TDOS at $E_F$. There is a pseudogap at the left of $E_F$ which indicates the stability of the structure [46]. The valence band just below $E_F$ extends from -5.4 to -1 eV. Here TDOS has significant contributions from Cr 3d and Co 3d states. In this band, little contribution comes from the Al atom. Here, strong hybridization of Co 3d and Cr 3d states to the TDOS below $E_F$ is observed. There is a peak above $E_F$ at an energy of 1.9 eV. This peak is due to sole contribution from Cr 3d orbital. The near half metallicity of Cr$_2$CoAl is evident from the band structure and DOS curves. The pressure dependent TDOS curve of Cr$_2$CoAl [Figure 5(c)] shows that the near half metallicity disappears at ~30 GPa because TDOS at $E_F$ is non-zero at this pressure for both up and down spin channels.

Electronic band structure of Cr$_2$MnAl is calculated at pressures up to 30 GPa at an interval of 10 GPa along the high symmetry directions $W$-$L$-$I'$-$X$-$W'$-$K$ in the first Brillouin zone. Figure 6 (a-d) and (e-h) represent the band structures of Cr$_2$MnAl for up and down spin, respectively. There is a band gap in the band structure for up spin channel. This implies that Cr$_2$MnAl is semiconducting in nature for one type of spin, namely, up spin. On the other hand, overlapping of the valence band and conduction band is observed from Figure 6(e) at $E_F$ in the band structure for other type of spin, namely, down spin. This indicates the metallic nature of Cr$_2$MnAl for down spin channel. Hence half metallicity of Cr$_2$MnAl is revealed from the band structures for up and down spin channels. This result is consistent with the available computational investigation [22]. The value of band gap of Cr$_2$MnAl at 0 GPa is 0.38 eV for up spin channel. The band gap decreases with increasing external pressure and become zero at pressure around 30 GPa. On the other hand, for down spin channel the metallic character of Cr$_2$MnAl is preserved up to 30 GPa. It seems that the half-metallicity of Cr$_2$MnAl disappears at around 30 GPa.

Figure 5(b) shows the TDOS and PDOS of Cr$_2$MnAl for up and down spin channels at zero pressure. The Fermi level is indicated by vertical broken line marked as red. The value of TDOS is zero for up spin which is evident from Figure 5(b). This implies that Cr$_2$MnAl is semiconducting in

| Compound  | $P$ (GPa) | $\rho$ (gm/cm$^3$) | $\nu_l$ | $\nu_u$ | $\nu_m$ | $E_F$ (eV) | $\theta_D$ (K) | Reference  |
|-----------|-----------|-------------------|---------|---------|---------|------------|--------------|------------|
| Cr$_2$CoAl | 0         | 6.671             | 26.5330 | 3.8120  | 4.3610  | 901.29     | This work    |
| 5         | 6.845     | 26.6475           | 3.8290  | 4.3810  | 920.95  |
| 10        | 6.955     | 28.1869           | 3.9298  | 4.4965  | 955.26  |
| 15        | 7.104     | 29.8928           | 4.0106  | 4.5892  | 968.89  |
| 20        | 7.219     | 30.7613           | 4.0910  | 4.6812  | 1019.57 |
| 25        | 7.337     | 31.0526           | 4.1599  | 4.7600  | 1047.97 |
| 30        | 7.457     | 31.9328           | 4.2219  | 4.8310  | 1075.16 |
| Cr$_2$MnAl | 0         | 6.042             | 19.8798 | 3.8083  | 4.3543  | 848.20     | This work    |
| 5         | 6.262     | 22.3659           | 3.9895  | 4.5625  | 910.23  |
| 10        | 6.426     | 24.1394           | 4.1235  | 4.7163  | 957.33  |
| 15        | 6.596     | 25.8294           | 4.2282  | 4.8266  | 998.98  |
| 20        | 6.737     | 27.0832           | 4.3136  | 4.9345  | 1033.61 |
| 25        | 6.881     | 28.2801           | 4.3780  | 5.0085  | 1064.04 |
| 30        | 7.030     | 29.1508           | 4.4259  | 5.0634  | 1091.14 |
nature for up spin. Above $E_F$, a peak is observed at 1.4 eV in which Cr 3d state contributes more than other states of Mn and Al atoms.

But the finite value of TDOS points out the metallic nature of Cr$_2$MnAl for other type of spin, namely, down spin. Hence the TDOS curve also confirms the half metallic behaviour of the compound Cr$_2$MnAl. For the down spin channel, the dominant contribution to the TDOS at $E_F$ comes from Cr 3d and Mn 3d states. The Al 3p state has almost no contribution to the TDOS at $E_F$. There is deep valley at the left of $E_F$ known as pseudogap indicates the structural stability of the structure [46]. There is a peak in the TDOS curve at about -2.2 eV which is originated from the

Figure 4. Band structure of Cr$_2$CoAl along the high symmetry directions W-L-$\Gamma$-X-W-K. Horizontal broken line (red colour) indicates the Fermi level. Calculated band structure for spin-up channel at pressures (a) 0 GPa, (b) 10 GPa, (c) 20 GPa and (d) 30 GPa. Band structure for spin-down channel at (e) 0 GPa, (f) 10 GPa, (g) 20 GPa and (h) 30 GPa.
hybridization of Cr 3d and Mn 3d states with the dominance of Cr 3d state. Two more peaks above \( E_F \) are seen at about 0.5 eV and 1.8 eV which are Cr 3d dominated. Moreover, the half metallicity of Cr\(_2\)MnAl is confirmed from both the band structure and TDOS curves. It is noteworthy that these interpretations of the band structure and TDOS curves are also helpful to explain the optical properties of Cr\(_2\)MnAl which will be discussed in Section 3.5.

In addition, the pressure dependence of TDOS of Cr\(_2\)MnAl [Figure 5(d)] shows that the TDOS at \( E_F \) for up spin channel changes from zero to finite value at around 30 GPa whereas TDOS at \( E_F \) for down spin channel is non-zero at pressures up to 30 GPa. Hence half metallicity of Cr\(_2\)MnAl is lost at ~30 GPa.

In order to observe the effect of Hubbard parameter (U), the band structure of Cr\(_2\)MnAl and Cr\(_2\)CoAl are also calculated by using GGA + U approximations as shown in Figures 7 and 8, respectively. The same approximations as shown in Figures 7 and 8, respectively. The same

3.5. Optical properties

Various energy dependent optical parameters such as the real and imaginary parts of dielectric constant, \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \), respectively, static refractive index \( n \), extinction coefficient \( k \), loss function \( L \), real part of the optical conductivity \( \sigma_{\text{r}} \), reflectivity \( R \) and the absorption coefficient \( \alpha \), are calculated at pressures up to 30 GPa at an interval of 10 GPa to study the response of a material to incident electromagnetic waves, namely, infrared, visible and ultraviolet radiations. These studies are helpful to judge the potential optoelectronic device applications. The calculated optical parameters for Cr\(_2\)MnAl and Cr\(_2\)CoAl at external pressures up to 30 GPa are presented in Figures 9, 10, 11, 12, 13, and 14. The local field effect is not included in this calculation. A plasma frequency of 3 eV, damping of 0.05 eV is used for the dielectric constant calculation [48]. The \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are connected with each other through Kramers Kronig relation.

The \( \varepsilon_2(\omega) \) is given by the equation [49]:

\[
\varepsilon_2(\omega) = \frac{2e^2}{\Omega c_0} \sum_{k, \mathbf{k}} \left( \psi^*_k(\mathbf{r}) \mathbf{u} \cdot \mathbf{r} \psi^+_k(\mathbf{r}) \right)^2 \delta(E_k^r - E_k^s - E)
\]  

(14)

where \( e \) is the electronic charge, \( \Omega \) is the volume of the unit cell, \( \mathbf{u} \) is the unit vector along the polarization of the incident electric field, \( \omega \) is the frequency of the photon, \( \psi_k^r \) and \( \psi_k^s \) are the wave functions for conduction and valence band electrons. The other optical constants are directly related to \( \varepsilon_2(\omega) \).

The static refractive index \( n(\omega) \), extinction coefficient \( k(\omega) \), absorption coefficient \( \alpha(\omega) \), loss function \( L(\omega) \), reflectivity \( R(\omega) \), and photodconductivity \( \sigma(\omega) \) can be calculated by using the equations [49, 50]:

Figure 5. TDOS and PDOS of the compounds (a) Cr\(_2\)CoAl and (b) Cr\(_2\)MnAl at 0 GPa, and TDOS of (c) Cr\(_2\)CoAl and (d) Cr\(_2\)MnAl at pressures from 0 to 30 GPa at an interval of 10 GPa. The vertical broken line (red colour) indicates the Fermi level. Solid and dashed lines indicate DOS for spin up and down channels, respectively.
\begin{align*}
n(\omega) & = \frac{1}{\sqrt{2}} \left[ (\epsilon_1(\omega))^2 + (\epsilon_2(\omega))^2 + \epsilon_1(\omega) \right]^{\frac{1}{2}} \\
n\omega(\omega) & = \sqrt{2}\omega \left[ (\epsilon_1(\omega))^2 + (\epsilon_2(\omega))^2 - \epsilon_1(\omega) \right]^{\frac{1}{2}} \\
L(\omega) & = \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2]^{\frac{1}{2}}} \\
\end{align*}

Figure 6. Band structure of Cr$_2$MnAl along the high symmetry directions W-L-$\Gamma$-X-W-K. Horizontal broken line (red colour) indicates the Fermi level. Calculated band structure for spin-up channel at pressures (a) 0 GPa, (b) 10 GPa, (c) 20 GPa and (d) 30 GPa. Band structure for spin-down channel at pressures (e) 0 GPa, (f) 10 GPa, (g) 20 GPa and (h) 30 GPa.
Figure 7. Band structure of Cr$_2$MnAl with DFT + U approximation along the high symmetry directions W-L'-X-W-K. Horizontal broken line (red colour) indicates the Fermi level. Calculated band structure for spin-up channel considering (a) $U = 0.5$ eV, (b) $U = 1.0$ eV and for spin-down channel considering (c) $U = 0.5$ eV, (d) $U = 1.0$ eV for both Cr and Mn atoms.

Figure 8. Band structure of Cr$_2$CoAl with DFT + U approximation along the high symmetry directions W-L'-X-W-K. Horizontal broken line (red colour) indicates the Fermi level. Calculated band structure for spin-up channel considering (a) $U = 0.5$ eV, (b) $U = 1.0$ eV and for spin-down channel considering (c) $U = 0.5$ eV, (d) $U = 1.0$ eV for both Cr and Co atoms.
\[ R(\omega) = \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \]  

\[ \sigma(\omega) = \frac{\omega \varepsilon_2}{4\pi} \]  

Figure 9 represents the variation of \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) with the energy of electromagnetic radiation at pressures from 0 to 30 GPa at an interval of 10 GPa. For metallic compounds, \( \varepsilon_1(\omega) \) should have large negative value. For both Cr\(_2\)MnAl and Cr\(_2\)CoAl, this behaviour is evident from the patterns shown in Figure 9. It is observed that there is a sharp decrease in \( \varepsilon_1 \) at about the energy in the range 2–3 eV which is consistent with the DOS curves for Cr\(_2\)MnAl and Cr\(_2\)CoAl. The relative height of the peaks at around 2 eV at 0 GPa are different for different compounds and the peak heights are seen to increase with pressure up to 30 GPa. The value of \( \varepsilon_2 \) at 0 GPa approaches zero at about 17 eV and 11 eV for Cr\(_2\)CoAl and Cr\(_2\)MnAl, respectively, which indicates the sharp decrease in absorption and reflectivity spectra as shown in Figures 11 and 13.

The static refractive index, \( n(\omega) \) and extinction coefficient, \( k(\omega) \), depend on the wavelength, i.e., energy of the incident radiation. Their dependence on energy of the incident radiation at pressure up to 30 GPa is shown in Figures 10 and 11. The energy dependence of \( n(\omega) \) and \( k(\omega) \) is very much similar to that of \( \varepsilon_2(\omega) \). The static refractive index has the high value of 84.7 and 84.5 at zero photon energy for Cr\(_2\)CoAl and Cr\(_2\)MnAl, respectively. Hence these materials are promising candidates for opto-electronic device. The static refractive index for Cr\(_2\)CoAl and Cr\(_2\)MnAl is roughly unchanged with increasing external pressure. There is a gradual decrease in \( n(\omega) \) with the energy and \( n(\omega) \) approaches zero at about 17 eV and 11 eV at 0 GPa for Cr\(_2\)CoAl and Cr\(_2\)MnAl, respectively. This feature is consistent with the dielectric function curves. The static refractive index has the link with the phase velocity of the electromagnetic radiation in the material.

Figure 10. Static refractive index of Cr\(_2\)MnAl and Cr\(_2\)CoAl at pressures from 0 to 30 GPa at an interval of 10 GPa.

Figure 11. Extinction coefficient \( (k) \) and absorption coefficient \( (\sigma) \) of Cr\(_2\)MnAl and Cr\(_2\)CoAl at pressures from 0 to 30 GPa at an interval of 10 GPa.

Figure 12. Loss function of Cr\(_2\)MnAl and Cr\(_2\)CoAl at pressures from 0 to 30 GPa at an interval of 10 GPa.
Figure 12 shows the variation of the loss function ($L$) of Cr$_2$CoAl and Cr$_2$MnAl with incident photon energy at various external pressures up to 30 GPa. The sharp peak located at 19 eV (16 eV) corresponds to the bulk screened plasma frequency, $\omega_p$, for Cr$_2$CoAl (Cr$_2$MnAl). The peaks shift towards higher photon energies in both compounds as the external pressure increases up to 30 GPa.

From the reflectivity spectrum of the compounds at pressures up to 30 GPa at an interval of 10 GPa (Figure 13), the high value of reflectivity, $R(\omega)$, is observed in the energy range 0–18 eV at 0 GPa. This property may present Cr$_2$MnAl and Cr$_2$CoAl as potential candidates to construct optoelectronic devices. A sharp decrease in the reflectivity at 0 GPa from high value is evident from Figure 13 at about 16 eV and 19 eV for Cr$_2$MnAl and Cr$_2$CoAl, respectively, which is consistent with the loss function spectrum as shown in Figure 12. The photon energy at which the sharp decrease in the reflectivity is observed shifts towards the higher photon energy with increasing external pressure. The effect of pressure on $R$ seems similar for both compounds.

Another indication of the metallic nature of the material Cr$_2$CoAl is obtained from the finite value of the photoconductivity at very small incident energy (Figure 14). Photoconductivity of both the Heusler compounds Cr$_2$CoAl and Cr$_2$MnAl increases gradually in the visible range of the electromagnetic spectrum from zero photon energy and reaches maximum at about 3 eV. Maximum photoconductivity of Cr$_2$MnAl is higher than that of Cr$_2$CoAl. The peak height at 3 eV for both the compounds increases with external pressure over the studied pressure range.

4. Conclusion

DFT based calculations are carried out on the study of hydrostatic pressure effect (up to 30 GPa) on the structural, elastic, mechanical, electronic and optical properties of the Heusler compounds Cr$_2$MnAl and Cr$_2$CoAl. Calculated ground state lattice constants of these compounds agree well with previous experimental and computational studies. The progressive decrease of lattice parameters and unit cell volume with pressure is an indication of structural stability of the studied compounds at elevated pressure up to 30 GPa. The absence of the imaginary frequency in our calculated phonon dispersion curves reveals the dynamical stability of these compounds at elevated pressure up to 30 GPa. The increase of elastic constants with pressure reveals the mechanical stability of these compounds in the considered pressure range. The calculated limiting values of Pugh’s ratio, Poisson’s ratio and Cauchy pressure indicates the brittleness of Cr$_2$MnAl while those indicate the ductility of Cr$_2$CoAl. The gradual increase of Debye temperature with hydrostatic pressure points out the rigidity of both compounds at elevated pressure.

Declarations

Author contribution statement

M. Jubair: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
A. M. M. Tanveer Karim, M. Nuruzzaman, M. A. K. Zilani: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.
M. Roknuzzaman: Performed the experiments; Analyzed and interpreted the data.

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Data will be made available on request.

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The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.
