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## Elastic and phonon properties of quaternary Heusler alloys CoFeCrZ (Z = Al, Si, Ga and Ge) from density functional theory

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The structural, elastic and phonon properties of the quaternary CoFeCrZ (Z = Al, Si, Ga and Ge) Heusler alloys have been investigated using the generalized gradient approximation method within density functional theory. The ground-state properties, including, lattice constant and bulk modulus are in good agreement with the available theoretical and experimental data. The elastic constants  $C_{ij}$  are computed using the stress–strain technique. The calculated results indicate that CoFeCrZ (Z = Al, Si, Ga and Ge) alloys are ductile materials. Debye temperatures are predicted from calculated elastic constants. The phonon dispersion relations of CoFeCrZ (Z = Al, Si, Ga and Ge) alloys are calculated for the first time using the density functional theory and the direct method with  $2 \times 2 \times 2$  supercell.

**Keywords:** quaternary Heusler alloys; *ab initio* calculation; elastic constants; phonon properties

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### 1. Introduction

In the past decades, the half-metallic Heusler compounds attracted great scientific interest because of their potential use in spintronic applications [1–4]. In these materials, the two spin bands have a completely different behaviour. Half-metallic Heusler compound is the metal for spin-up electrons and semiconductors for spin-down electrons. The half-metallic Heusler compound hybrids between normal metals and semiconductors. The majority of spin band (referred to also as spin-up band) is crossed by Fermi level as in a normal metal while the Fermi level falls within a gap in the minority spin band (spin-down band) as in semiconductors. The origin of interest in magnetic properties of the Heusler compounds is the prediction of half-metallic ferromagnetism in MnNiSb by de Groot et al. [5] and in Co<sub>2</sub>MnSn by Kübler et al. [6]. Similarly, Plogmann et al. [7] found a half-metallic ferromagnet-like behaviour for Co-based Heusler alloys. The Co-based Heusler alloys are of particular interest, because they show a comparatively high Curie temperature and varying magnetic moments [8]. Quaternary Heusler compounds exhibit a half-metallic behaviour. Half-metallic Heusler Co<sub>2</sub>Cr<sub>1-x</sub>Fe<sub>x</sub>Al compounds were studied using the density functional theory within the generalized

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gradient approximation (GGA) [9]. For the quaternary  $\text{Co}_2\text{Cr}_{1-x}\text{FeAl}$  Heusler alloys, Wurmehl et al. [10] calculated the electronic structure and spectroscopic properties using the fully relativistic Korring–Kohn–Rostocker method, and measured magnetic properties by X-ray absorption. Their results suggest that the half-metallic ferromagnet-like behaviour of  $\text{Co}_2\text{Cr}_{1-x}\text{Fe}_x\text{Al}$  is mainly characterized by Co. On the other hand, Karthik et al. [11] investigated the structure, magnetic properties and spin polarization of the quaternary  $\text{Co}_2\text{Cr}_{1-x}\text{FeAl}$  Heusler alloys. For  $\text{CoFeCrAl}$ , the structural and magnetic properties were studied by Luo et al. [12] using *ab initio* method and SQUID magnetometer, respectively. Quaternary half-metallic Heusler alloy  $\text{CoFeCrAl}$  with high spin polarization have been reported very recently [13]. They found the energy gap value of 0.41 eV around the Fermi level in the bands of minority spin electrons. Xu et al. [14] performed pseudopotential method to study the electronic properties of the  $\text{CoFeCrGa}$  Heusler compound. Gao et al. [15] found that  $\text{CoFeCrGa}$  and  $\text{CoFeCrGe}$  are nearly half-metals, while  $\text{CoFeCrAl}$  and  $\text{CoFeCrSi}$  exhibit excellent half-metallicity using full-potential linearized augmented plane wave method implemented with the Wien2 K package [16].

In this work, we have aimed at to provide some additional information to the exhibit data on the elastic and phonon properties of  $\text{CoFeCrZ}$  ( $Z = \text{Al}, \text{Si}, \text{Ga}$  and  $\text{Ge}$ ) alloys. The full phonon dispersion curves are necessary for a microscopic understanding of the lattice dynamics. Knowledge of the phonon spectrum plays a significant role in determining various material properties, such as phase transition, thermodynamic stability, transport and thermal properties.

## 2. Computational methods

The calculations were performed within the density functional theory, as implemented in the MedeA-Vasp package [17,18] with the projected augmented wave [19]. For the exchange-correlation functional, the GGA of Perdew–Burke–Ernzerhof (GGA-PBE) [20] was chosen. An energy cut-off 500 eV was found to be adequate for the spin-polarized calculation of the structural, elastic and phonon properties. The electronic iterations convergence is  $1.00 \times 10^{-05}$  eV using the Normal (blocked Davidson) algorithm and reciprocal space projection operators. The  $k$ -point sampling was done on a  $4 \times 4 \times 4$  Monkhorst and Pack [21] grid for  $\text{LiMgPdSn}$ -type crystal structure. The Fermi distribution function with a smearing parameter of 0.2 eV was used to integrate the bands at Fermi level. Elastic constant was obtained using the method of least-squares fit [22] as implemented in the MedeA-MT module. The elastic properties ( $G$ ,  $E$ ) were calculated from the Hill value, which is a geometric mean of the Voigt and Reuss values. The Hill values were used in the estimation of transverse ( $v_t$ ), longitudinal ( $v_l$ ) and average ( $v_m$ ) sound velocities, and the Debye temperatures [23]. Phonon dispersion curves were calculated using the MedeA-PHONON [24] module with the forces calculated with the Vasp. We used a  $2 \times 2 \times 2$  supercell containing 4096 atoms for  $\text{LiMgPdSn}$ -type crystal structure.

## 3. Results and discussion

Heusler alloys are the ternary intermetallic compounds with the composition  $\text{X}_2\text{YZ}$  in  $\text{L2}_1$  structure with space group of  $\text{Fm-3 m}$ , where X and Y are transition elements, and Z

is a main group element (III, IV and V group elements). When one of X atoms is substituted for another transition metal element, a quaternary Heusler compounds  $XX'YZ$  with the space group of F-43 m is generated. The quaternary Heusler compounds crystallize in the cubic structure (F-43 m, space group No. 216) with LiMgPdSn as prototype, as shown in Figure 1 [25,26]. The calculated structural parameters ( $a$  and  $B$ ) are given in Table 1, in comparison with the theoretical results and experimental data. Generally, our lattice parameters are in good agreement with those found theoretically reported in Refs. [12,14,15]. The predicted equilibrium lattice parameter is 1% smaller than the experimental data [13] for CoFeCrAl. It is noticed that the lattice parameter for the four Heusler alloys are comparable with slight decreases from CoFeCrGa to CoFeCrGe to CoFeCrAl to CoFeCrSi. CoFeCrSi has the highest value of the bulk modulus. It is noted that the bulk modulus  $B$  decrease in magnitude in the following sequence: CoFeCrSi  $\rightarrow$  CoFeCrAl  $\rightarrow$  CoFeCrGe  $\rightarrow$  CoFeCrGa, i.e. in inverse sequence to  $a$ .

The total magnetic moments ( $M_t$ ) for the four alloys are listed in Table 1. Our calculations show that CoFeCrAl, CoFeCrSi, CoFeCrGa and CoFeCrGe have total magnetic moments of 2.01, 2.99, 2.09 and 3.01  $\mu_B$  per formula unit, respectively. Our total magnetic moments are in excellent agreements with those of Gao et al. [15] using the GGA method and Luo et al. [12] using the local density approximation method.

Elastic constant can provide a link between the mechanical and dynamical behaviour of the crystals. The elastic constants  $C_{ij}$  contain some of the more important information that can be obtained from ground-state total energy calculations. The  $C_{ij}$  can be used to check the phase stability of the studied compounds, and provide an estimation of the strength and indirectly their melting temperature [27]. To the best of our knowledge, there are no experimental or theoretical data for the elastic constants of these Heusler alloys mentioned in the literature. So, our results can provide reference data for future investigations. It can be observed that CoFeCrSi possesses the highest elastic constants among the studied alloys (Table 1). The mechanical stability of these compounds has been analysed in terms of their elastic constants. For cubic crystals, the conditions for mechanical stability are given by Born and Huang [28].

$$C_{44} > 0, (C_{11} - C_{12})/2 > 0 \text{ and } B = (C_{11} + 2C_{12})/3 > 0$$

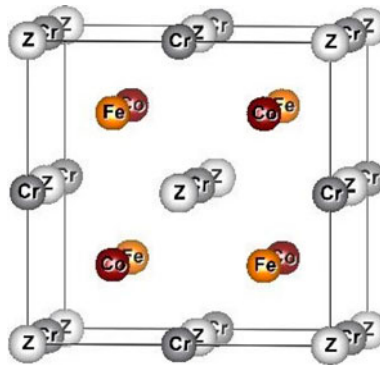


Figure 1. Crystal structure of quaternary Heusler alloys.



From Table 1, we see that these criteria are verified. As a result, we conclude that all the alloys are stable in the LiMgPdSn-type crystal structure. Pugh's  $B/G$  ratio empirical criterion [29] is one of the widely used criteria to provide information about brittle (ductile) nature of materials. If  $B/G > 1.75$ , the ductile behaviour is predicted; otherwise, the material behaves in a brittle manner. According to the calculation results in Table 1, the  $B/G$  ratios of all CoFeCrZ ( $Z = \text{Al, Si, Ga}$  and  $\text{Ge}$ ) Heusler alloys are higher than 1.75, i.e. indicating a ductile nature of these materials. The Young's modulus  $E$  characterizes the stiffness of a material. When it is higher for a given material, the material is found to be stiffer. From our results of  $E$ , it can be stated that CoFeCrAl, CoFeCrSi and CoFeCrGa are stiffer alloys than CoFeCrGe alloy. The Debye temperature is an important parameter in characterizing lattice vibrations of a solid. It plays a key role in the discussions of the temperature dependence of the electrical resistivity in metals. The average velocity  $v_m$  calculated from transverse velocity  $v_t$  and longitudinal velocity  $v_l$  is used to determine the Debye temperature [23,30]. The obtained values of the transverse, longitudinal and average sound velocities ( $v_t$ ,  $v_l$  and  $v_m$ , respectively), and the Debye temperature  $\theta_D$  for CoFeCrZ ( $Z = \text{Al, Si, Ga}$  and  $\text{Ge}$ ) Heusler alloys are also given in Table 1. The calculated Debye temperature and average sound velocity of CoFeCrAl are larger than those of CoFeCrZ ( $Z = \text{Ga, Ge}$  and  $\text{Si}$ ), while the  $B/G$  ratio is smaller. The properties of the four alloys are quite similar apart from the mass of  $Z$  elements, which is the dominating factor leading to smaller sound velocities in CoFeCrGe compared to the other calculated alloys. Unfortunately, as far as we know, there are no data available related to these properties in the literature for CoFeCrZ ( $Z = \text{Al, Si, Ga}$  and  $\text{Ge}$ ).

Figure 2 shows the calculated phonon dispersion curves of CoFeCrZ ( $Z = \text{Al, Si, Ga}$  and  $\text{Ge}$ ). As expected for LiMgPdSn-type crystal structure (space group F-43 m) with four atoms in the primitive cell, the phonon dispersion curve exhibits 12 branches, three acoustic (one longitudinal (LA) and two transverse (TA)) and nine optical branches. It should be noted that phonon dispersion curves of CoFeCrZ ( $Z = \text{Al, Si, Ga}$  and  $\text{Ge}$ ) alloys have not yet been theoretically and experimentally studied to the knowledge of the authors. All phonon modes exhibit positive frequencies, suggesting that CoFeCrZ ( $Z = \text{Ge}$  and  $\text{Al}$ ) lattice is dynamically stable. For CoFeCrAl, a soft transverse acoustic mode (TA) phonon mode has been found along  $\Gamma-L$  directions. Similar features have been observed for  $\text{Fe}_2\text{CrAl}$  Heusler alloy that were clearly discussed in our previous work [31]. At the phonon of the TA mode for CoFeCrGa alloy,  $\Gamma-L$  directions become imaginary. The phonon band structure for CoFeCrGa in the LiMgPdSn-type crystal structure shows that it is dynamically unstable. Note that CoFeCrSi has instabilities throughout the entire Brillouin zone. The imaginary phonon modes may lead to the distortion of the crystal. The highest optical phonon modes for these alloys are well separated from other optical phonon modes. These optical modes come from vibrations of the  $Z$  ( $Z = \text{Al, Si, Ga}$  and  $\text{Ge}$ ) atom. For CoFeCrAl, the phonon energies of the lowest transverse optical and longitudinal acoustical (LA) modes are found to be 14.68 and 14.18 meV, respectively, at the X point. The optical mode frequencies at the  $\Gamma$  point are 17.84, 19.16 and 44.38 meV for CoFeCrAl; -0.09, 22.09 and 38.95 meV for CoFeCrSi; 14.01, 15.39 and 29.91 meV for CoFeCrGa; and 27.08, 28.06 and 30.74 meV for CoFeCrGe, respectively.

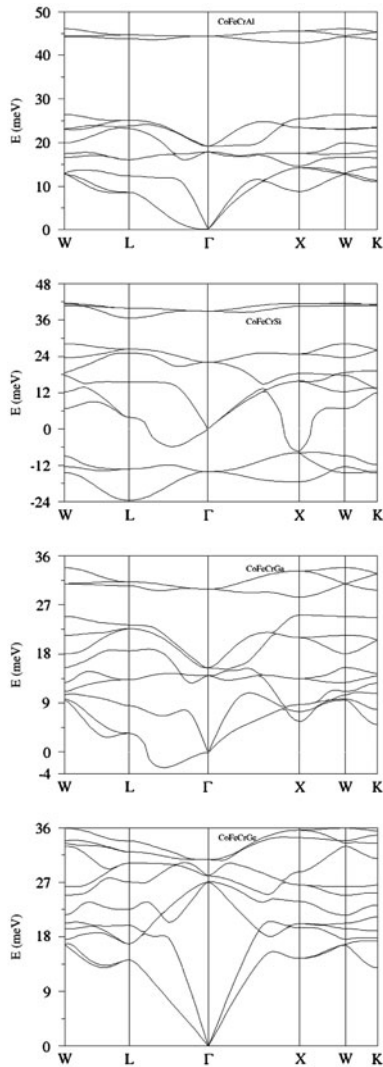


Figure 2. Calculated phonon dispersion curves for CoFeCrZ ( $Z = \text{Al, Si, Ga and Ge}$ ) quaternary Heusler alloys along lines of high symmetry in the Brillouin zone.

#### 4. Conclusion

In conclusion, the structural, elastic and phonon properties of the quaternary CoFeCrZ ( $Z = \text{Al, Si, Ga and Ge}$ ) have been investigated by DFT. The phonon and elastic properties of the systems under study are reported for the first time. Our calculated lattice parameters and total magnetic moments are in good agreement with the theoretical data. A numerical first principles method was used to calculate the elastic properties. The average sound velocity decreased from CoFeCrAl to CoFeCrGe due to the increase in the mass of Z ( $Z = \text{Al, Si, Ga and Ge}$ ) elements. The LiMgPdSn-type crystal structure

of CoFeCrGe is found to be stable, according to the phonon calculation. We found that the LiMgPdSn-type crystal structure is also dynamically unstable for CoFeCrGa and CoFeCrSi. The obtained results are very interesting from an application and scientific point of view, and we hope that our results can provide reference data for future experimental investigations in this field.

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