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Structural, electronic and vibrational properties of ordered intermetallic alloys CoZ (Z = Al, Be, Sc and Zr) from first-principles total-energy calculations

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Self-consistent band calculations on four intermetallic compounds of the CsCl structure are presented. The calculations were performed employing the self-consistent ultrasoft pseudopotential method based on the density functional theory, within the local density approximation and the generalized gradient approximation. The calculations predicted that the equilibrium lattice constants are in excellent agreement with the experiment for CoAl and are 1% smaller than experimental values for CoBe, CoSc and CoZr, respectively. In the present study, ordered CoAl do not show any magnetic moment, whereas the other three compounds have moderate magnetic moments of about 0.2 and 0.7 Bohr magnetons (μ_B) per atom. The elastic constants are calculated using two approaches, the energy-strain method and the use of phonon dispersion curves. The values obtained from the two methods are in reasonable agreement for the studied intermetallic compounds CoZ (Z = Al, Be, Sc and Zr). The brittleness and ductility properties of CoZ (Z = Al, Be, Sc and Zr) are determined by Poisson's ratio σ criterion and Pugh's criterion. The calculated elastic constants satisfy the mechanical stability criterion and the ductility of CoZr and CoSc is predicted by Pugh's criterion. The band structure and density of states, and phonon dispersion curves have been obtained and compared with the available experimental results as well as with existing theoretical calculations. We studied and discussed the position of Fermi level for the selected four intermetallic compounds.

Keywords: density-functional theory; elastic constants; ductility; intermetallic alloys; vibrational properties

1. Introduction

During the past few decades, there have been intense studies on intermetallic compounds. These compounds are widely used for many applications such as modern

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gas turbines, aircraft combustion zone turbine blades, high temperature furnaces, etc. The importance of these compounds is due to high melting temperatures and better oxidation resistance [1,2].

Substantial recent efforts have been devoted to the search for new classes of intermetallic compounds [3–7]. In the past, intermetallics with outstanding physical properties had already triggered the development of functional materials like, for example, superconductors (Nb_3Sn), shape memory alloys (NiTi), high permeability materials (Ni_3Fe), permanent magnets (Co_5Sm) [2] and hydrogen storage materials (FeTi, CoTi and CoZr) [8]. However, at present, they are not used in practice independently as structural materials for being extremely brittle at and below room temperature. Also, their low fracture toughness at room temperature limits their fabricability during manufacture and their reliability in service. Many of these materials might become more practical if they could be put into a metastable, chemically disordered phase that it is easier to machine or forge at room temperature to put it into nearly net shape. Therefore, the investigation on ductility of the intermetallic compounds is a very important subject from the point of view of their practical use.

A new class of fully ordered, completely stoichiometric intermetallic compounds, YL (L = Ag, Cu, Rh, In), MAg (M = Ce, Er, Nd), NCu (N = Dy, Er, Ho) and ErG (G = Au, Ir) have been identified. These compounds are formed by combining a rare earth element with certain main group or transition metals. The resulting binary compounds have *B*2 crystal structure. The discovery of ductility in these compounds suggests that many of the other *B*2 compounds might also be ductile [9,10]. These compounds were different in that they are single-phase, fully ordered, and tested in air of normal humidity at room temperature. Subsequent research on these rare-earth *B*2 intermetallics has been done to investigate their slip system [10,11], dislocation behaviour [10–12], fracture toughness [10], oxidation behaviour [13] and strain rate sensitivity. Other intermetallics have been shown to be ductile when the composition was off-stoichiometric; for example, Ni_3Al, Ni_3Ga and Co_3Ti [14]. NiAl's tensile ductility was increased to 2% when the composition was changed to 50.3 at.% Aluminum. This ductility was further increased to 40% when strained at 873 K [15]. Carefully work-hardened, annealed and stoichiometrically balanced CoZr shows 23% tensile ductility at room temperature when tested in vacuum [8].

Co-based alloys have important advantageous applications in many fields such as magnetic materials and potential high-temperature materials [16,17]. Especially, the class of co-based compounds with rare earth elements is of particular interest due to their outstanding magnetic properties [18]. An extensive experimental and theoretical search of intermetallic CoAl has been done [19–23]. High-resolution data on the directional Compton profiles of FeAl, CoAl and NiAl single crystals were presented [24]. Optical properties of transition metal aluminides were studied by the linear muffin-tin orbital (LMTO) method [25] and by the linearized-augmented Plane-Wave method [26] for NiAl and CoAl. The experimental absorption maxima have been found to be correlated to the band structure of these alloys [20]. The equation of state and all zero-pressure elastic moduli for CoAl have been calculated [27] also using the FLAPW method. NMR measurements have been made on seven cubic equiatomic group-VIII aluminides. The results have shown that charge was transferred from Al to the transition metal. In CoA1, there is evidence for the presence of localized magnetic moments due to an excess of Co over the stoichiometric amount [28]. The differences

in electronic structure of $B2$-type (CsCl) transition-metal aluminides (FeAl, CoAl and NiAl) have been investigated by comparing the data obtained using electron energy-loss spectroscopy with theoretical calculations of the spectra [29]. The ideal tensile strengths of the $B2$-type CsCl transition-metal aluminides, FeAl, CoAl and NiAl, have been investigated using an *ab initio* electronic structure total energy method. The three materials exhibit dissimilar mechanical behaviours under the simulated ideal tensile tests along [0 0 1], [1 1 0] and [1 1 1] directions. FeAl is the weakest in tension along [0 0 1], whereas CoAl and NiAl are stronger in the same direction [30]. The constitutional and thermochemical information of the Co–Zr system is modelled using the CALPHAD method to obtain a reliable thermodynamic description of the system. Results from *ab initio* calculations are used to aid the optimization of Gibbs energy descriptions of $CoZr_3$, $CoZr_2$ and BCC-$B2$ phases [31]. Investigations of CoTi [32,33], CoZr [34,35] and CoHf [36], show that these intermetallics also deform by activation in $\langle 1\,0\,0\rangle$ slip direction. This means they are likely to be highly ordered and yet they also show positive temperature dependence in the flow stress. However, very little is known on the physical properties of CoZ (Z = Be, Sc and Zr) compounds especially the mechanical and vibrational ones in the ordered $B2$ phase. All of them are metallic. To the best of our knowledge, there are no reports on the study of vibrational properties of these compounds. In an effort to understand them in the present work, the first principle calculations are performed to investigate the fundamental properties of the CoZ (Z = Al, Be, Sc and Zr) compounds with $B2$ structure including total energy, lattice constant, electronic band structure, density of states, mechanical properties, vibrational properties and ductility as well.

This paper is organized as follows. Section 2 is devoted to the description of our calculational methods. We discuss the results of our calculations in Section 3 for the structural and vibrational properties of CoZ (Z = Al, Be, Sc and Zr) compounds, including comparison with experiment. The electronic structure of these intermetallics is examined. A summary is given in Section 4.

2. Structure and method of calculation

2.1. *Total-energy calculation*

An intermetallic compound is loosely defined as a compound consisting of two or more metals. Binary intermetallics comprise compounds of two metals (or a metal and a semimetal) whose crystal structures are different from those of the elements. Many intermetallics with the approximate composition AB crystallize in the $B2$ structure also known as CsCl structure. Examples are CoZ (Z = Al, Be, Sc and Zr). In the completely ordered state, A atoms occupy one cubic primitive sublatice and B atoms the other. This means that each A atom is surrounded by eight B atoms on the nearest neighbour sites and vice versa. Intermetallic compounds display several features, like a lack of simple bonding or valence rules and closed-shell states [37], delocalized bonding of the valence electrons [37] and complex bonding, depending on the elements involved, the structure and the stoichiometry [37].

The first-principles studies of the CoZ (Z = Al, Be, Sc and Zr) compounds were performed by employing the self-consistent ultrasoft pseudopotential method [38] based on the density functional theory, within the local density approximation (LDA) and the

generalized gradient approximation (GGA), incorporated into the the quantum-Espresso code [39]. We employed the Ceperley–Alder functional as parameterized by Perdew and Zunger [40] and also the Perdew–Burke–Ernzerhof [41,42] for the exchange-correlation potential. The energy cutoff for the expansion of the eigenfunctions was set to 40 Ry. The electronic charge density was evaluated up to the kinetic energy cut-off 400 Ry. A grid of $(10 \times 10 \times 10)$ k-points generated was symmetry reduced and used to sample the irreducible wedge of the first Brillouin zone. Integration up to the Fermi surface was performed using the Methfessel–Paxton smearing technique [43] with smearing parameter $\sigma = 0.02$ Ry. When exploring the electronic structure, a finer grid $(35 \times 35 \times 35)$ was chosen to generate a high-quality charge density. With these choices, the total energy was converged to 1 mRy per atom. Having obtained self-consistent solutions of Kohn–Sham equations, the lattice-dynamical properties were calculated within the framework of the self-consistent density functional perturbation theory [44]. To obtain complete phonon dispersions and density of states, eight dynamical matrices were calculated on a $(4 \times 4 \times 4)$ q-point mesh. The dynamical matrices at arbitrary wave vectors were evaluated using Fourier deconvolution on this mesh. The ground state of each compound was found by minimizing the total energy as a function of the lattice parameters.

2.2. *Elastic properties*

The elastic constants C_{ij} contain some of the more important information which 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, the melting temperature [45]. To obtain the elastic constants of these compounds with cubicstructure we have used a numerical first principles calculation by computing the components of the stress tensor e for small strains, using the method reported in ref [46]. It is well known that a cubic crystal has only three independent elastic constants.

The theoretical elastic constants are calculated from the energy variation by applying small strains to the equilibrium lattice configuration. The elastic energy under strain is given by:

$$\frac{\Delta E}{V} = \frac{V}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} e_i e_j \tag{1}$$

where V is the volume of the undistorted lattice cell, ΔE is the energy increment by the strain with vector $e = (e_1, e_2, e_3, e_4, e_5, e_6)$ and C is the matrix of elastic constants. The primitive vectors a_i $(i = 1, 2, 3)$ of crystals are transformed to the new vectors under the strain by

$$\begin{pmatrix} a'_1 \\ a'_2 \\ a'_3 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \times (I + \varepsilon) \tag{2}$$

where ε is the strain tensor. It relates to the strain vector e by

$$\varepsilon = \begin{pmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{pmatrix} \tag{3}$$

for the strain under hydrostatic pressure $e = (\delta, \delta, \delta, 0, 0, 0)$, which transforms the total energy to:

$$\frac{\Delta E}{V} = \frac{9}{2} B \delta^2 \tag{4}$$

where B is the bulk modulus, $B = (C_{11} + 2C_{12})/3$.

Application of [1 1 1] shear strain $e = (0, 0, 0, \delta, \delta, \delta)$ changes the total energy from its initial value as follows:

$$\frac{\Delta E}{V} = \frac{3}{2} C_{44} \delta^2 \tag{5}$$

Finally, for the last type of deformation, we use the volume-conserving rhombohedral strain tensor given by $e = (\delta, \delta, (1+\delta)^{-2} -1, 0, 0, 0)$ which transforms the total energy as:

$$\frac{\Delta E}{V} = 6C'\delta^2 + O(\delta^3) \tag{6}$$

where C' is defined by $C' = (C_{11} - C_{12})/2$.

In this study, we calculated 21 sets of $\frac{\Delta E}{V}$ by varying δ from -0.02 to 0.02 in steps of 0.002. These data were fitted by a quadratic polynomial and then the relevant elastic constant is obtained from the coefficient of the corresponding quadratic term in Equations (4)–(6).

To gain more insight about the elasic properties of the compounds under investigation, we used the method explained in [47] to calculate C_{11}, C_{12} and C_{44}. The elastic constants for CoZ (Z = Al, Be, Sc and Zr) compounds can also be extracted from the slopes of the acoustic phonon branches for small wave vectors [47]. We obtained the sound velocities $v_{LA}^{[0\,0\,1]}$ and $v_{TA}^{[0\,0\,1]}$, for TA and LA branches and $v_{LA}^{[1\,1\,0]}$, for the LA phonon branch along the [0 0 1] and [1 1 0] direction, respectively, using the Equations (7)–(9).

$$v_{LA}^{[0\,0\,1]} = \sqrt{\frac{C_{11}}{\rho}} \tag{7}$$

$$v_{LA}^{[0\,0\,1]} = \sqrt{\frac{C_{44}}{\rho}} \tag{8}$$

$$v_{LA}^{[0\,0\,1]} = \sqrt{\frac{(C_{11} + C_{12} + 2C_{44})}{2\rho}} \tag{9}$$

where ρ is the mass density of the CoZ (Z = Al, Be, Sc and Zr) compounds.

The shear modulus G of a cubic structure is given by:

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \tag{10}$$

The anisotropy factor A is given by:

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \tag{11}$$

As A approaches unity the crystal becomes isotropic. We also list some auxilary quantities which are often quoted in the literature. The Young's modulus for an isotropic solid is related to B and G by the formula:

$$E = \frac{9BG}{3B + G} \tag{12}$$

Poisson's ratio is also of interest

$$\sigma = \frac{1}{2} \left(1 - \frac{E}{3B} \right) \tag{13}$$

3. Results and discussion

3.1. *Total-energy calculations: equilibrium lattice determination*

Ordered phase calculations of CoZ (Z = Al, Be, Sc and Zr) compounds would give information which can be used as a starting point for understanding the properties of the corresponding disordered phases. It has been found that the CoZ (Z = Al, Be, Sc and Zr) compounds were stable in *B*2 phase [27,48].

The total energy as a function of unit-cell volume around the equilibrium cell volume V_0 for CoZ (Z = Al, Be, Sc and Zr) compounds was calculated for *B*2 phase. We determined a set of total energies $E_i = E(V_i)$ and used several volumes which are within 10–30% of the expected equilibrium volume. Then the calculated total energies were fitted to Murnaghan's equation of state [49] to obtain the ground-state properties. The calculated structural parameters of CoZ (Z = Al, Be, Sc and Zr) phases are listed in Table 1, compared with the available experimental data and other theoretical results [30,48,50–55]. It is evident from Table 1 that the computed values of equilibrium lattice constants are consistently overestimated by about 0% for CoAl using GGA and underestimated by about 3% using LDA. The calculations predicted the equilibrium lattice constants are 1% smaller than experiments for CoBe, CoSc and CoZr. The values of bulk moduli calculated from the second derivative of total energy are about 200 GPa for

Table 1. Calculated lattice constant *a*, bulk modulus *B* and its pressure derivative *B′*, and the total magnetic moment for CoZ (Z = Al, Be, Sc and Zr) compounds, compared with the available experimental and theoretical data.

Alloys	References	*a* (Å)	*B* (GPa)	*B′*	M_t (μ_B)
CoAl	This Work (GGA)	2.860	177.4	4.52	0
	This Work (LDA)	2.772	206.5	4.68	0
	[30] VASP (LDA)	2.800	157.0	–	–
	[50] Exp.	–	162.0	–	–
	[51]	–	107.1	–	–
	[52] Exp.	2.850	–	–	–
	[53] Exp.	2.860	–	–	–
	[48] LMTO	2.814	211	–	0
	[54]TBLMTO-ASA LDA	2.836			
CoBe	This Work (LDA)	2.582	216.9	4.43	0.3
	[51]	–	177.8	–	–
	[52] Exp.	2.611	–	–	–
CoSc	This Work (GGA)	3.113	103.4	5.42	0.22
	[51]	–	54.6	–	–
	[52] Exp.	3.145	–	–	–
CoZr	This Work (GGA)	3.186	137.1	6.79	0.74
	[55] Exp.	–	140.0	–	–
	[51]	–	78.0	–	–
	[52] Exp.	3.197	–	–	–

CoAl and CoBe and smaller for CoSc and CoZr. They are given in Table 1. For CoAl, our estimate of 177.4 GPa using GGA and 206.5 GPa using LDA are greater than the experimental value (162 GPa) [50] and also the calculated value using pseudopotential method (157.0 GPa) [30]; and however agree quite well with the TB-LMTO theoretical value (211 GPa) [48].

On the other hand, there are roughly 21, 87.37 and 75% overestimation of the theoretical values of the bulk moduli for CoBe, CoSc and CoZr by the present calculations. For CoZr, we found a value of 2% difference from the experimental value reported in ref [55]. It is interesting to note that the lattice parameter decreases when we move from CoZr, to CoSc, to CoAl and to CoBe. On the other hand, the bulk modulus increases as we go from CoSc, to CoZr, to CoAl and to CoBe.

It should be noted that for CoZ (Z = Be, Sc and Zr), the total energy reduces as we switch on spin polarization; but, for CoAl, no such magnetic effect is manifested. There is common agreement in the literature that the perfectly ordered compound CoAl is nonmagnetic [55,56]. In the present study, ordered CoAl does not show any magnetic moment, whereas the other compounds have moderate magnetic moments ranging from 0.2 to 0.7 μ_B per atom. In another study, ordered CoAl and NiAl have not shown any magnetic moments, whereas for FeAl a magnetic moment of about 0.7 μ_B per atom has been found [48]. In Table 1, we present the total magnetic moments of CoZ (Z = Al, Be, Sc and Zr). We find that the total magnetic moment per formula units increase when we move from CoAl, to CoSc, to CoBe and to CoZr.

3.2. *Total-energy calculations: elastic properties and mechanical stability*

knowledge of the elastic constants is important for a variety of reasons. At the most fundamental level, the adiabatic elastic constants are given by the second derivatives of the internal energy with respect to strain and thus are related to interatomic potentials. They are also related to the thermal properties of a solid through the Debye theory. In cubic materials, only three independent elastic constants are needed, C_{11}, C_{12} and C_{44}. So, the study of the second-order elastic constants (C_{11}, C_{12} and C_{44}) and their pressure derivatives at 0 K are quite important for understanding the nature of the interatomic forces. Hence, we have computed the elastic constants of CoZ (Z = Al, Be, Sc and Zr) compounds with $B2$ structure using the Equations 4–6. They are listed in Table 2, together with data from available experimental and other calculations for comparison [27].

It is seen that the departures of most of our theoretical elastic constants from the calculated data reported by Mehl [27] are between 0.5–16% using GGA and about 30% using LDA for CoAl. However, for CoZr, our estimated values of elastic contants agree very well with those reported in [57] with a difference less than 6%. To the best of our knowledge, no experimental values for the elastic constants of these compounds have appeared in the literature; so, our results for $B2$ phase can serve as a reference for future investigations.

C_{11}, C_{44} and C_{12} were calculated from our phonon dispersion curves and listed in Table 2. These values are in reasonable agreement with our *ab initio* results for the studied intermetallic compounds CoZ (Z = Al, Be, Sc and Zr).

Mechanical stability of these compounds has been analysed in terms of their elastic constants. The conditions for mechanical stability for cubic crystals [58] are given by

$$C_{44} > 0, \quad (C_{11} - C_{12})/2 > 0 \quad \text{and} \quad B = (C_{11} + 2C_{12})/3 > 0 \qquad (14)$$

Table 2. Calculated elastic constants C_{ij} (GPa), for $B2$ phase of CoZ (Z = Al, Be, Sc and Zr) compounds using two approximations: I: Energy-strain approach, II: Phonon dispersion curves approach.

Alloys	References	B (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
CoAl	(GGA) I.	173.23	271.62	124.03	130.65
	(GGA) II.	156.58	302.09	83.82	137.45
	(LDA) I.	206.50	342.14	140.37	160.18
	(LDA) II.	179.48	380.04	79.05	160.52
	[27]	157.00	257.00	107.00	130.00
CoBe	I.	217.60	315.10	168.80	167.00
	II.	197.90	238.10	177.80	156.00
CoSc	I.	103.90	189.50	61.20	51.00
	II.	105.10	211.20	52.10	47.00
CoZr	I.	134.00	201.40	100.30	39.20
	II.	142.10	189.00	118.70	41.90
	[57]		205.00	107.00	49.00

It is seen from Table 2 that these criteria were verified; so, we conclude that all the compounds are stable in the $B2$ phase.

It is acknowledged that the bulk modulus B measures the hardness in an indirect way. From Tables 1 and 2, we see that the bulk modulus of CoBe is the largest one and the smallest one is that of CoSc.

In order to further analyse the mechanical properties of CoZ (Z = Al, Be, Sc and Zr) compounds, brittleness and ductility properties have also been studied by using the shear modulus to bulk modulus B/G ratio and Poisson's ratio σ. According to Pugh [59], if B/G ratio is smaller than 1.75, the material behaves in a brittle manner; otherwise, the material behaves in a ductile manner. It is clearly seen from Table 3 that CoZr and CoSc are ductile materials; however, CoAl and CoBe (according to the first approach I) are brittle. This is in good agreement with the results found by Kaneno et al. and Wollmershauser et al. for CoZr [8,57]. According to Frantsevich et al. [60], Poisson's ratio can also be used to distinguish the brittleness from ductility in metal and intermetallic materials. Metals having Poisson's ratios around 1/3 are ductile, whereas metals having Poisson's ratios less than 1/3 are inferred as being brittle. On the basis of the Poisson's ratio shown in Table 3, the brittleness and ductility properties of CoZ (Z = Al, Be, Sc and Zr) determined by Poisson's ratio σ criterion are in good agreement with the results estimated by the B/G ratio, except for CoSc compound which was found to be a brittle material. Young's modulus E 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 the material is. The largest Young's modulus among the compounds in Table 3 is that of CoAl so we conclude that the CoAl is the stiffest one. Also, the anisotropy factor A is a measure of the degree of elastic anisotropy in the crystal (see Table 3) and we note that the compounds studied in this work are strongly anisotropic elastically. Our calculated values of

Table 3. Calculated shear modulus G (GPa), B/G, Young's modulus E (GPa), Poisson's ratio σ, anisotropy factor A and Debye temperature Θ_D (K) for $B2$ phase of CoZ (Z = Al, Be, Sc and Zr) compounds.

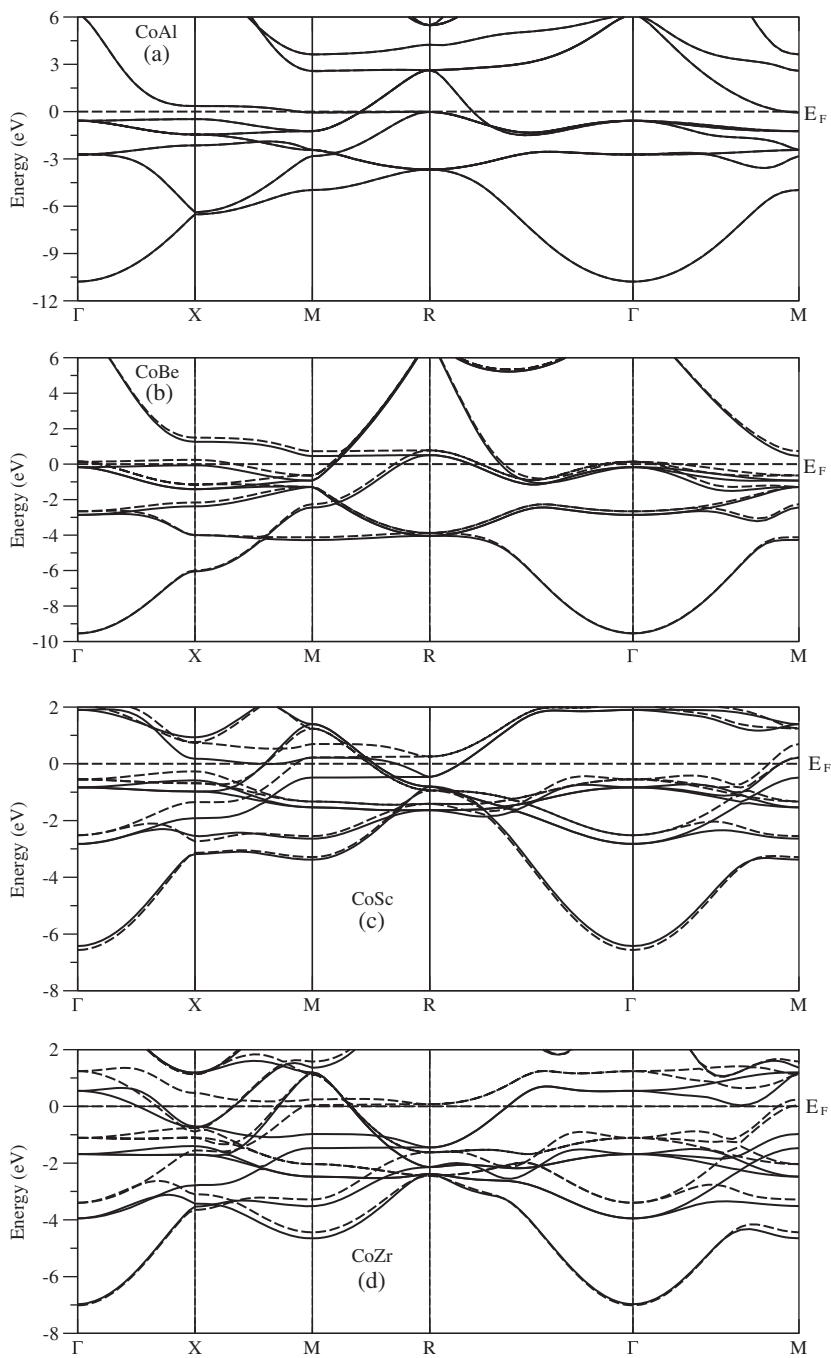| Alloys	References	G	B/G	Θ_D	E	σ	A
CoAl	(GGA) I.	107.91	1.61	510.99	268.07	0.24	1.77
	(GGA) II.	126.12	1.24	–	298.28	0.18	1.26
	(LDA) I.	136.46	1.51	547.91	335.48	0.23	1.59
	(LDA) II.	156.51	1.15	–	363.79	0.16	1.07
CoBe	I.	129.46	1.68	697.07	324.11	0.25	2.28
	II.	105.56	1.87	–	268.87	0.27	5.17
CoSc	I.	56.26	1.85	361.26	142.97	0.27	0.80
	II.	60.02	1.75	–	151.27	0.26	0.59
CoZr	I.	43.74	3.06	280.8	118.34	0.35	0.78
	II	39.20	3.63	–	107.70	0.37	1.19
	[55] Exp.	49.2			132	0.34	
	[57]					3	1

Figure 1. Calculated electronic band structure for CoZ (Z = Al, Be, Sc, Zr) in the *B*2 phase. The solid line represents spin-up and the dashed line represents spin down.

shear modulus, Young's modulus and Poisson's ratio for CoZr are in good agreement with the experimental ones of [55].

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. It is proportional to the sound velocity. Our calculated values of Θ_D are also listed in Table 3.

3.3. Electronic and vibrational properties

In order to estimate the influence of spin polarization on energy, spin-polarized band structure calculations of the ordered CoZ (Z = Al, Be, Sc and Zr) alloys have been made. All exhibit a metallic behaviuor as shown in Figure 1(a–d) where one can notice that the energy bands cros s the Fermi level. It is clearly seen that they present similar features for low energies. We confirmed from the band structure calculations that the ordered stoichiometric CoAl is non-magnetic (Figure 1(a)). It is characterized by a narrower d band than that found in pure Co [26]. The overlap of d-wave functions of the Co atoms is reduced because being next-nearest neighbours to each other on a simple cubic sublattice with a lattice constant of 2.86, 2.582, 3.113 and 3.186 Å for CoA1, CoBe, CoSc and CoZr, respectively, the distance between Co atoms is larger than in pure Co (2.412 Å), leading to the band narrowing. On the other hand, the hybridization with the s and mostly the p levels of Z, which lie above the Fermi level, leads to bonding states in the lower part of the d band and to antibonding states in the region above E_F. Since the bonding states are mostly centred at the Co site, the number of Co d electrons considerably increases and the number of Z s and p electrons decreases compared

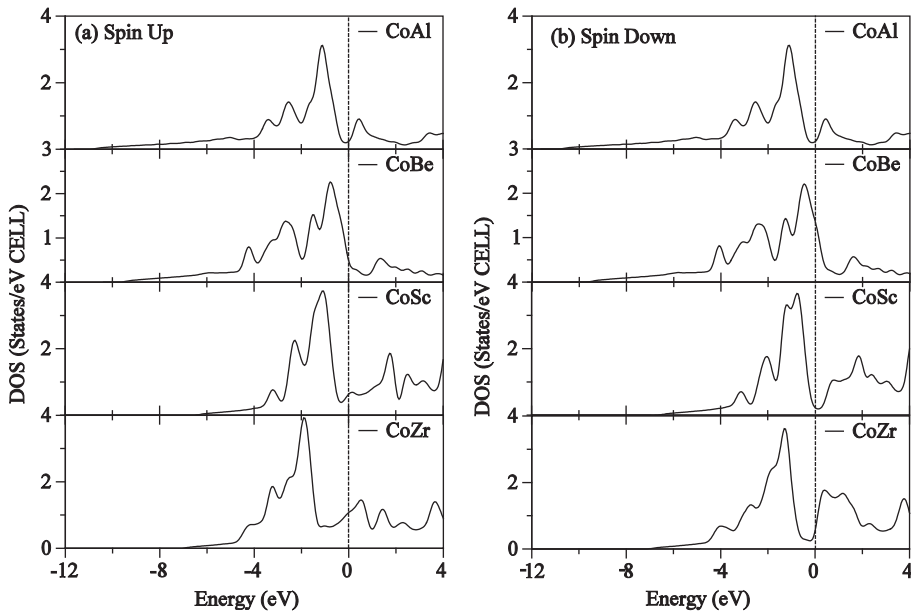
Figure 2. The total DOS for CoZ (Z = Al, Be, Sc, Zr) in the B2 phase. (a) Spin-up, (b) Spin-down.

to the situations in elemental Co and *Z*, respectively (Figure 2). A further consequence of the strong hybridization is that the tendency for magnetism is suppressed completely in CoAl and appeared slightly in the other compounds ranging from 0.2 to $0.7\,\mu_B$, as it is shown in Figure 3.

As a preliminary comparison of the electronic structure in the series, we analyse important features of the calculated DOS. The total DOS distributions in the CoAl and CoBe in one hand and CoZr and CoSc in the other hand are very similar. The Fermi energy lies in a region of low density of states, between a high peak and a smaller one. The Fermi level of CoAl resides in the 'pseudo gap' which separates the bonding and anti-bonding states (Figure 3(a)). The Fermi level falls within the bonding states (Figure 3(b)) for CoBe and electron structure analysis reveals the mechanism for its instability: the bonding states are only partially filled. CoZr, in contrast, pushes the Fermi level towards the anti-bonding peak and it is located at the upper band composed
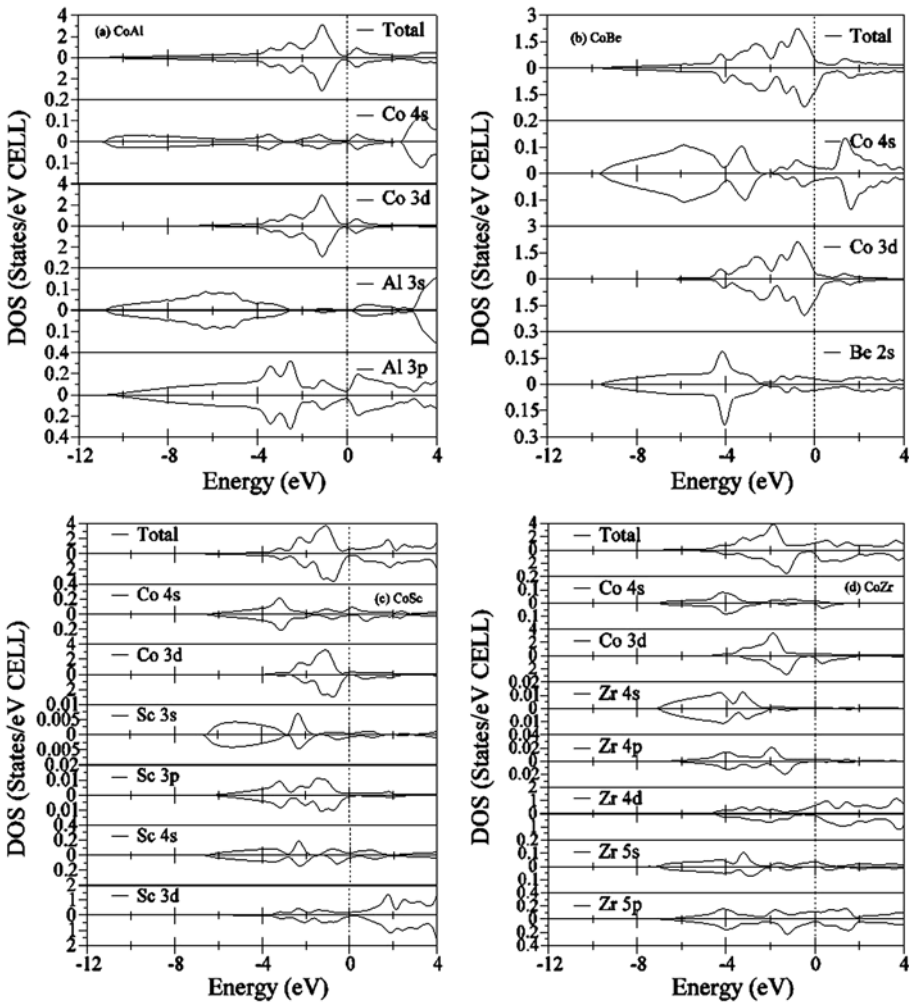

Figure 3. Calculated partial and total DOS for CoZ (Z = Al, Be, Sc and Zr) in the *B*2 phase.

of the anti-bonding states (Figure 3(d)). The Fermi level lies in the region with the low density of the nonbonding states. All bonding states are thus fully occupied, and their density greatly exceeds the density of the non-bonding states. Therefore, the Zr–Co interaction in ZrCo results in the strong bonding and high compound stability, since the bonding is dominated by the Zr–Co nearest-neighbour interaction. For CoSc, the Fermi level crosses the buttom of the anti-bonding peak for the majority of electrons and resides in the pseudogap for the minority of spins (Figure 3(c)). Filling the anti-bonding states would result in the energy increase of the system and hence weakens the stability of the bonding. The tendency of increasing lattice constants from CoAl to CoZr is consistent with this analysis.

Generally speaking, the bands near the Fermi level are formed mainly by the transition metal Co d-states for CoZ compounds. The DOS profiles of CoAl agree with previous calculations using other computational techniques such as ultra-soft pseudopotentials [30] and LMTO-ASA method [48]. However, for CoZr and CoSc compounds, the bands are dominated by Co d-states under the Fermi level and just above it by a hybridization of Co d-states with Zr d- and Sc d-states. The density of states at Fermi

Table 4. Calculated total and local partial density of states at Fermi energy $N(E_F)$ for CoZ (Z = Al, Be, Sc and Zr) compounds.

| Alloys			$N\downarrow(E_F)$ (states/eV cell)	$N\uparrow(E_F)$ (states/eV cell)	References
CoAl	Co	4s	0.0044344	0.0044545	
		3d	0.1781280	0.1781320	
	Al	3s	0.0019291	0.0019192	This work
		3p	0.0394276	0.0396280	
	Total		0.2239191	0.2241336	
			0.61	0.61	[48]
			0.596	0.596	[27]
			0.44	0.44	[61]
CoBe	Co	4s	0.0273370	0.0229430	
		3d	1.2390000	0.4010400	This work
	Be	2s	0.0332390	0.0304920	
	Total		1.2995760	0.4544750	
CoSc	Co	4s	0.0125128	0.0817884	
		3d	0.0789240	0.3152200	
	Sc	3s	0.0008629	0.0003446	
		3p	0.0009892	0.0011609	This work
		4s	0.0372384	0.0230176	
		3d	0.0601504	0.1818280	
	Total		0.1906777	0.6033595	
CoZr	Co	4s	0.0064875	0.0137416	
		3d	0.3833350	0.2711460	
	Zr	4s	0.0000955	0.0007881	This work
		4p	0.0004471	0.0019256	
		4d	0.1257950	0.6213790	
		5s	0.0012854	0.0360832	
		5p	0.0340562	0.1147708	
	Total		0.5515017	1.0598343	
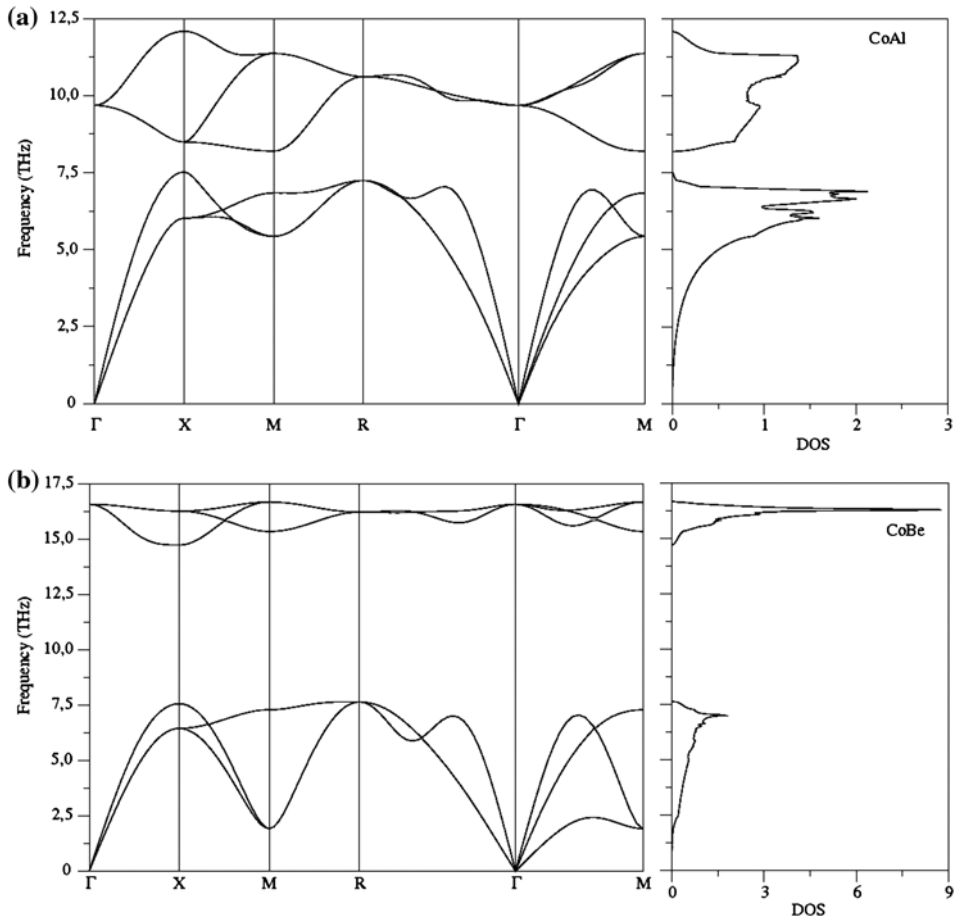
Figure 4. Calculated phonon dispersion curves and phonon DOS for CoZ (Z = Al, Be, Sc, Zr) in the *B*2 phase along several lines of high symmetry in the Brillouin zone.

energy $N(E_F)$ which shows the degree of metallicity of these materials CoZ (Z = Al, Be, Sc and Zr) is shown in Table 4. It is clearly seen from Table 4 that for CoAl compound, $N(E_F)$ is smaller than the values found in ref [27,48]. This is explained by the fact that we used a pseudopotential method however in ref [27,48,61], the value of $N(E_F)$ is calculated using a full potential method. Unfortunately, no experimental data are available for CoAl.

Phonon dispersion curves and density of states for CoZ (Z = Al, Be, Sc and Zr) in the *B*2 phase are shown in Figure 4. The primitive cell of the CoZ contains two atoms, leading to a total of six phonon branches. As CoZ (Z = Al, Be, Sc and Zr) have metallic character in the *B*2 phase, the longitudinal optical and transverse optical (TO) phonon modes are triply degenerate, and there is no splitting between these modes at the zone centre. Because of the symmetry, the distinct number of phonon branches is reduced along the principal symmetry directions Γ–X and M–R–Γ. For CoAl and CoBe, gaps between the acoustical and optical phonon branches exist and this is due to a large mass difference between Co and Al (Be) atoms. For CoSc and CoZr, this gap is absent (see
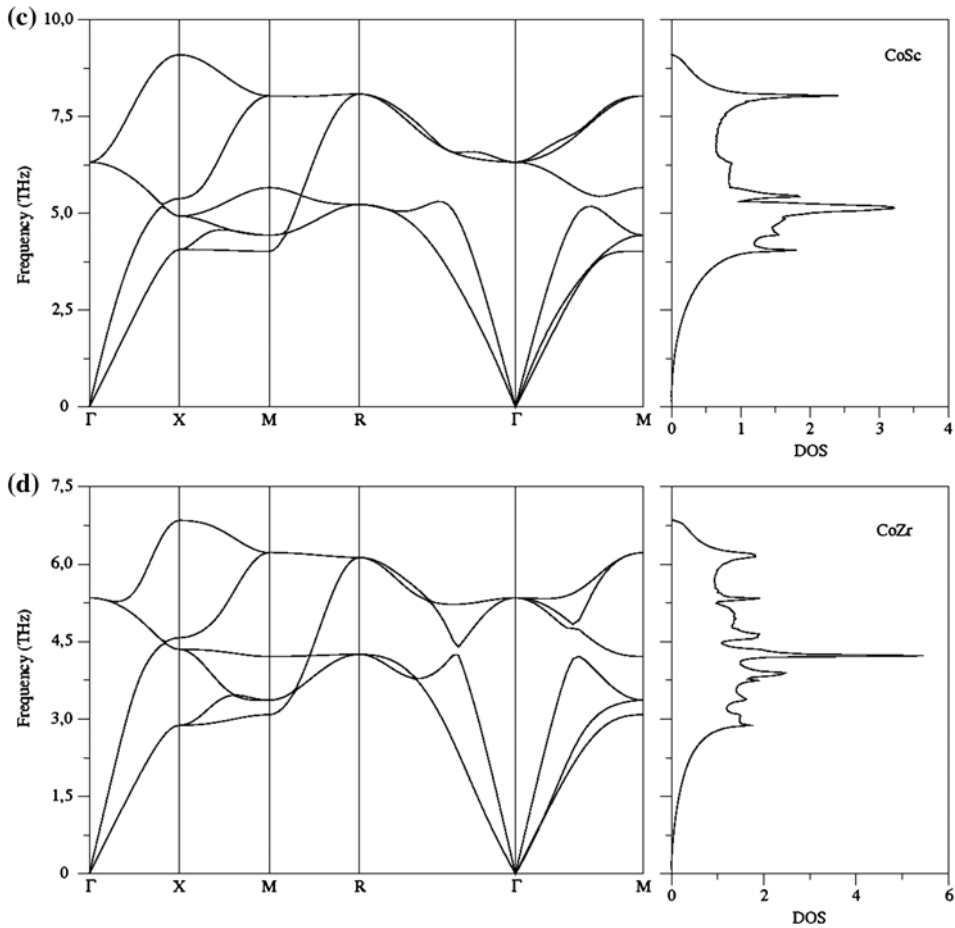
Figure 4. (Continued).

Figure 4(c–d)) since there is a considerable overlap between the TO and longitudinal acoustical (LA) phonon branches. Acoustic and optic phonon modes obtained within GGA and LDA approximation for CoAl show similar trends. We observe the peaks distributed mainly around two acoustical frequency ranges in CoAl (GGA). The distributed peaks between 5.20 and 6.40 THz are due to TA (X), LA (M) and TA (M) modes. The peaks between 6.50 and 7.60 THz are also obtained which may be assigned to LA (X), TA (M) and LA (M) phonons. In the phonon density of states, the band gap between the acoustic and optic branches of CoAl (CoBe) is around 0.72 THz by GGA, and 0.60 THz by LDA (7.13 THz). The zone-centre optical phonon modes of CoAl are calculated to be 9.68 THz (GGA) and 10.30 THz (LDA). These modes of CoZ (Z = Be, Sc and Zr) are calculated to be 16.57, 6.32 and 5.35 THz, respectively.

4. Conclusion

We have performed self-consistent total-energy calculations in the framework of density functional theory using the LDA and the GGA to determine the equations of state and

the elastic constants of CoZ (Z = Al, Be, Sc and Zr) in the *B*2 (cesium chloride) phase. The lattice constants and bulk moduli were determined and are in excellent agreement with the available experimental data. It is interesting to note that the lattice parameter decreases when we move from CoZr, CoSc and CoAl to CoBe; on the other hand, the bulk modulus increases from CoSc, CoZr and CoAl to CoBe. The compounds CoBe, CoSc and CoZr retain a magnetic moment of 0.3, 0.22 and 0.74 μ_B per atom, respectively; however, the magnetic moment of CoAl is totally quenched due to the *d*-band population. Because the new technological applications demand the increased use of metals which are strong, stiff, and ductile at high temperatures, we have also studied the mechanical properties of these compounds. The elastic constants are calculated using two approaches, the energy-strain method and the phonon dispersion curves. The values obtained from the two methods are in reasonable agreement for the studied intermetallic compounds CoZ (Z = Al, Be, Sc and Zr). The calculated elastic constants satisfy the mechanical stability criterion and the ductility of CoZr, and CoSc is predicted by Pugh's criterion. The brittleness and ductility properties of CoZ (Z = Al, Be, Sc and Zr) determined by Poisson's ratio σ criterion are in good agreement with the results estimated by the B/G ratio except for CoSc compound which was found to be a brittle material. The band structure and densities of states DOS for the four alloys were analysed and compared. Furthermore, the position of Fermi level is discussed. Finally, the phonon dispersion curves and density of states for CoZ (Z = Al, Be, Sc and Zr) were presented and discussed. It is found that for CoAl and CoBe, gaps exist between the acoustical and optical phonon branches due to a large mass difference between Co and Al (Be) atoms. This gap is absent for CoSc and CoZr. From the phonon density of states, the band gap between the acoustic and optic branches of CoAl (CoBe) is around 0.72 THz (GGA) and 0.60 THz (7.13 THz) using LDA.

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