

First-Principles Study on the Structural, Electronic, Magnetic and Thermodynamic Properties of Full Heusler Alloys Co_2VZ ($Z = \text{Al}, \text{Ga}$)

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We report on the investigation of the structural and physical properties of the Co_2VZ ($Z = \text{Al}, \text{Ga}$) Heusler alloys, with L2_1 structure, through first-principles calculations involving the full potential linearized augmented plane-wave method within density functional theory. These physical properties mainly revolve around the electronic, magnetic and thermodynamic properties. By using the Perdew–Burke–Ernzerhof generalized gradient approximation, the calculated lattice constants and spin magnetic moments were found to be in good agreement with the experimental data. Furthermore, the thermal effects using the quasi-harmonic Debye model have been investigated in depth while taking into account the lattice vibrations, the temperature and the pressure effects on the structural parameters. The heat capacities, the thermal expansion coefficient and the Debye temperatures have also been determined from the non-equilibrium Gibbs functions. An application of the atom in molecule theory is presented and discussed in order to analyze the bonding nature of the Heusler alloys. The focus is on the mixing of the metallic and covalent behavior of Co_2VZ ($Z = \text{Al}, \text{Ga}$) Heusler alloys.

Key words: FP-LAPW, Heusler compounds, magnetic properties, thermal properties

INTRODUCTION

Recently, half-metallic ferromagnetic materials have been extensively studied both theoretically and experimentally due to their great potential application for many engineering fields.^{1,2} These compound materials have the property of high spin polarization, where the majority and minority spin bands are metallic and semiconducting, respectively,

with an energy gap located at the Fermi level.³ They can act as spin filters thus providing current, and are, consequently, key materials for spin-dependent phenomena in spintronics, which is considered as an emerging field in nanoscale electronics which uses the spin of electrons, rather than an electric charge, to encode and process data.^{1–3} On the other hand, the existence of martensitic transition in the Heusler alloys also makes them particularly attractive for actuation devices and smart materials, in addition to nonvolatile magnetic random access memories (MRAM) and magnetic sensors.^{4–6}

(Received January 28, 2016; accepted August 5, 2016)

Half-Heusler compounds having the chemical formula XYZ and crystallize mainly in the face-centered cubic C1b structure, with the space group F-43 m.⁷ In this structure, X, Y and Z atoms occupy the sites (1/4,1/4,1/4), (0,0,0) and (1/2,1/2,1/2), respectively, while the (3/4,3/4,3/4) site is empty. In addition, the half-metal (HM) part with the half-Heusler structure often exhibits a high Curie temperature,^{8,9} and, at the same time, their lattices match well with many semiconductor substrates such as MgO and GaAs.¹⁰

Groot and coworkers¹¹ first introduced the concept of half-metallic ferromagnets in 1983, following their investigation of band structure calculations in NiMnSb and PtMnSb half-Heusler compounds. Furthermore, half-metallic compounds have been found theoretically in various materials, including ferromagnetic metallic oxides,¹² dilute magnetic semiconductors,¹³ zincblende compounds,¹⁴ full-Heusler compounds¹⁵ and half-Heusler compounds.¹⁶

The Co₂VZ (Z = Al, Ga) alloy investigated in the present paper is a full-Heusler-type half-metallic ferromagnet (HMF), and is particularly suitable for applications such as magnetic MRAMs and/or current-perpendicular-to-plane (CPP) spin-valve GMR heads.^{17,18} Despite the serious demand motivated by their numerous potential applications, accurate calculations of its mechanical properties remain challenging. Indeed, while the number of researches related to the magnetic properties of the Co₂VZ (Z = Al, Ga) full-Heusler alloys is considerable, only very few studies have been conducted on their thermal and electronic charge properties.¹⁹ In addition, a systematic study of the topology of the electron density for Co₂VAl and Co₂VGa full-Heusler alloys seems also to be lacking.

In this paper, we explore the structural, electronic, magnetic and thermodynamic properties of the Co₂VZ (Z = Al, Ga) compounds by using first-principles calculations based on density functional theory (DFT). We have first found that the lattice constants and spin magnetic moments, as calculated by the Perdew–Burke–Ernzerhof parametrization of the generalized gradient approximation (PBE-GGA) method, totally agree with the experimental data. Second, the thermal effects using the quasi-harmonic Debye model were investigated with respect to the lattice vibrations, while the effects of both temperature and pressure on the structural parameters, heat capacities, thermal expansion coefficient and Debye temperatures, were determined from the non-equilibrium Gibbs functions. The local bonding properties were also investigated by means of two different approaches, namely, the atom in molecule theory (AIM)²⁰ and the electron localization function (ELF) methods.²¹ Our work constitutes a step forward toward the clear understanding of the chemical bonds and cohesion of full-Heusler alloys materials.

Computational Details

To calculate the electronic structure of the Co₂VZ (Z = Al, Ga) full-Heusler alloys, we performed the DFT within the framework of the FP-LAPW implanted in the Wien2k code.^{22–24} For the exchange and correlation potential, the PBE-GGA was used.^{25,26} The multipole expansion of the crystal potential and the electron density within muffin-tin (MT) spheres were cut at $l = 10$. Non-spherical contributions to the charge density and potential within the MT spheres were considered up to $l_{\max} = 6$. The cutoff parameter is $R_{\text{mt}} \cdot K_{\max} = 7$. In the interstitial region, the charge density and the potential are expanded as a Fourier series with wave vectors up to $G_{\max} = 12 \text{ a.u.}^{-1}$. The MT radii (R_{MT}) values are assumed to be 2.21 a.u., 2.21 a.u., 2.08 a.u. and 2.06 a.u. for Co, V, Al and Ga atoms, respectively. Using the energy eigenvalues and eigenvectors at these points, the density of states is determined by the tetrahedral integration method.²⁷

We have chosen a Debye-like model as a simple way to consider the vibrational motion of the lattice. While retaining the simplicity of the Debye model, we have followed a quasi-harmonic approach, making the Debye temperature, $\theta(V)$, dependent upon the volume of the crystal. A reasonable alternative was to consider the isotropic approximation.²⁸ We apply here the quasi-harmonic Debye model, implemented in the pseudo-code Gibbs.^{29–33} Doing so, we could calculate the thermodynamic quantities at any temperature and pressure from the calculated E–V data at $T = 0$ and $P = 0$. In addition, the elastic constants could also be calculated. Thermal properties could be determined from the quasi-harmonic Debye model. To undertake these investigations, ab initio calculations were performed with the FP-LAPW method in order to study the structural, magnetic, bonding and thermodynamic properties of Co₂VAl and the Co₂VGa in their L2₁ phase.

RESULTS AND DISCUSSION

Crystal Structure

As mentioned in the “[Introduction](#)”, the Heusler alloys have been found to crystallize in the L2₁ structure and have a stoichiometric composition of X₂YZ,³⁴ where X and Y are transition metal elements, and Z is a group III, IV or V element (in the present study, X = Co; Y = V and Z = Al and Ga). The full-Heusler structure consists of four penetrating face-centered cubic sublattices in which the X atoms occupy the (1/4,1/4,1/4) and (3/4, 3/4,3/4) sites, the Y atom the (0, 0, 0) site, and the Z atom the (1/2, 1/2, 1/2) site in Wyckoff coordinates. Figure 1a and b shows the crystal structure of the Co₂VAl and the Co₂VGa compounds.

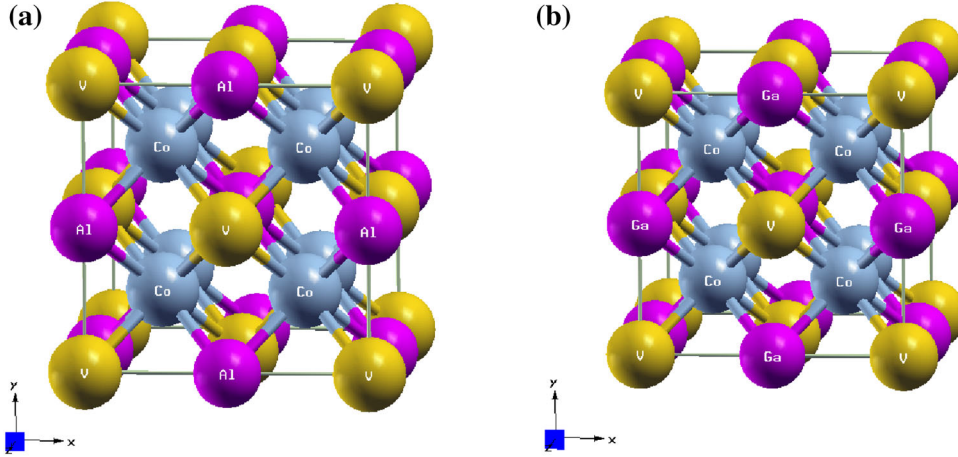


Fig. 1. Crystal structure of (a) Co_2VAl (b) and Co_2VGa Heusler alloys.

Table I. Equilibrium parameters of the Co_2VAl and the Co_2VGa : lattice constant a , and bulk modulus B

x	Lattice parameter a (Å)			Bulk modulus B (GPa)
	Our work	Exp.	Other cal.	Our work
Co_2VAl	5.7599	5.770 ^a	5.772 ^b , 2.891 ^c , 5.80 ^d , 5.76 ^e , 5.738 ^f , 5.754 ^g , 5.770 ^h , 6.076 ⁱ	197.4706
Co_2VGa	5.7673	5.786 ^a	5.779 ^b , 5.794 ^c , 5.78 ^d , 5.754 ^f	203.7825

^aRefs. 44 and 45. ^bRef. 39. ^cRef. 42. ^dRef. 36. ^eRef. 37. ^fRef. 38. ^gRef. 40. ^hRef. 43. ⁱRef. 41.

Total Energy and Lattice Parameter

To determine the equilibrium lattice constant and to discover how the total energy varies with the cell volume, we performed structural optimizations on both the Co_2VAl and Co_2VGa Heusler compounds. The total energy dependence on the cell volume is fitted by the Murnaghan equation of state (EOS) given by³⁵:

$$E_T(V) = \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] + E_0 - \frac{V_0 B_0}{B'_0 - 1}$$

where B_0 is the bulk modulus, B'_0 is the bulk modulus derivative, and V_0 is the equilibrium volume.

Table I summarizes the obtained results which are found to be in a good agreement with many other theoretical studies^{36–45} and also with the available experimental data.^{44,45} The calculated lattice parameters for the two compounds are found to agree well with the experimental measurements as performed in Refs. 44 and 45 and also with the theoretical values of Refs. 37–39. To the best of our knowledge, there are no available experimental or theoretical data in the relevant literature allowing a comparison with the specific results obtained on bulk modulus. Figure 2a and b displays the total energies dependence on the cell volume for the investigated Heusler compounds.

Magnetic Properties

Table II summarizes our calculated magnetic moments of the Co_2VGa and Co_2VAl compounds. We included, for comparison, the calculation results obtained in Refs. 39–41 and 44–46.

The total spin magnetic moment of the interstitial region increases from the vanadium ion with a small contribution of Co, Al and Ga sites for both compounds. The Al and Ga atoms have a small spin moment parallel to those of Co atom occupying the X sites in the lattice constant. The majority of the Heusler alloys compounds are well known for their magnetic behavior.^{36–43} Our calculated magnetic moments are compared with the experimental measurements of Refs. 44 and 45 and also with those predicted by computational methods.^{39–41} The calculated total magnetic moment is found to be of 55 and 2.00 μB per unit cell, which is mostly located in the Co atom for Co_2VAl and Co_2VGa , respectively.

Electronic Band Structure and Density of States

We calculated the electronic band structures along the high symmetry directions—in the first Brillouin zone—for the majority and minority spin, as depicted in Fig. 3a and b. We found that the minority spin of Co_2VAl and Co_2VGa exhibited a metallic nature, while the minority spin exhibited

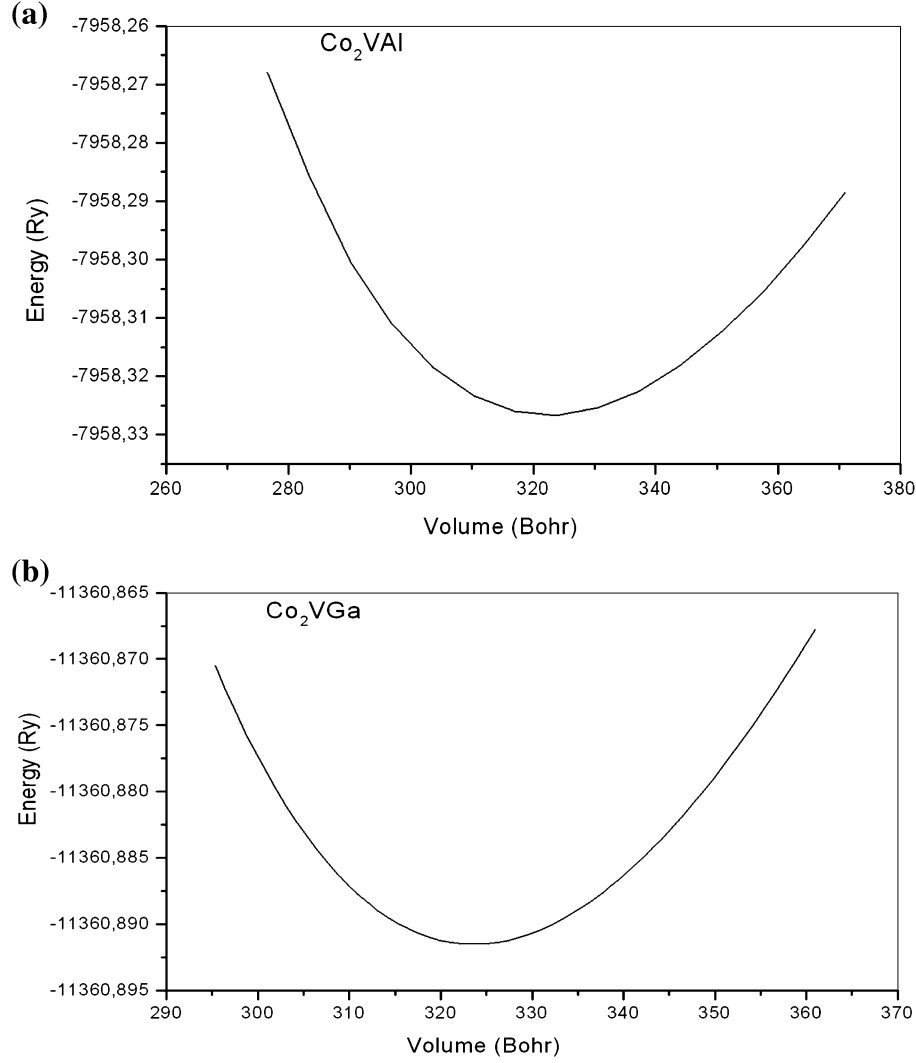


Fig. 2. Variation of the total energy E_{tot} (relative to that of the $L2_1$ phase) versus the unit cell volume for (a) Co_2VAI (b) and Co_2VGa using GGA calculation adjusting by the Murnaghan equation.

Table II. Total and partial magnetic moments of the Co_2VAI and the Co_2VGa compounds

Compound	M_{tot}	M_{Co}	M_{V}	M_{Z}
Co_2VAI				
Our work	1.55	0.596	0.327	-0.002
Exp.	1.65 ^b			
Other cal.	1.99 ^a , 1.93 ^c , 1.95 ^d , 2.00 ^e , 1.966 ^f	0.94 ^a , 0.86 ^c , 0.9782 ^f	0.22 ^a , 0.23 ^c , 0.1389 ^f	-0.03 ^{a,c} , -0.024 ^f
Co_2VGa				
Our work	2.00	1.052	0.122	-0.016
Exp.	1.95 ^b			
Other cal.	2.00 ^a	0.98 ^a	0.15 ^a	-0.02 ^a

^aRef. 38. ^bRefs. 44 and 45. ^cRef. 46. ^dRef. 39. ^eRef. 40. ^fRef. 41.

an indirect (Γ -X) band gap of about 0.3 eV for the Co_2VAI and 0.1 eV for the Co_2VGa . Therefore, our results reveal that Co_2VAI and Co_2VGa alloys clearly exhibit half-metallic (HM) properties.

In order to understand the electronic structure, we used the PBE-GGA to calculate the total and partial density of states (DOS and PDOS) for the spin-up (majority spin) and the spin-down (minority

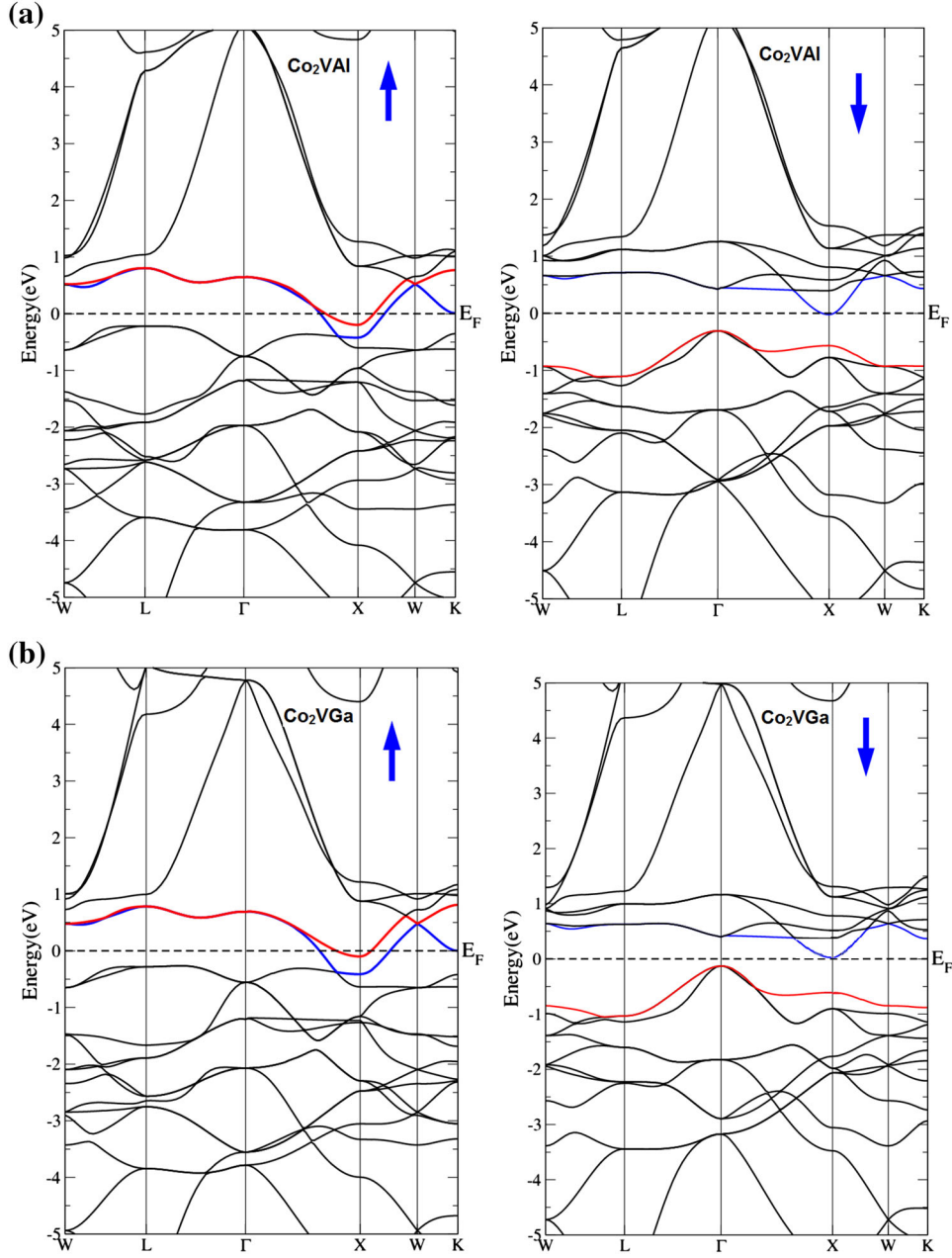


Fig. 3. The band structure for the majority-spin (left) and the minority-spin (right) of (a) Co_2VAI (b) and Co_2VGa alloys.

spin) configurations of the Co_2VAI and Co_2VGa . The obtained results are presented in Fig. 4a and b, and show that these compounds exhibit half-metallic (HM) behavior, thus confirming our previous findings presented in Fig. 3a and b. It is worth noting here that the minority spin gap mainly originates from the hybridization of the $d-d$ orbitals of the transition metal atoms. We should also emphasize that the density of states at the Fermi level (for the majority spin) is formed by the vanadium-3d and the cobalt-3d states.

Our results agree with the calculations of Bentouaf et al.⁴⁷ who studied the Co_2VSi full-Heusler compound.

Bonding Properties–AIM Theory Analysis

The analysis of bonding interaction from the charge density distribution $\nabla\rho(r)$ alone to identify the nature of chemical bonding may be not sufficient and even misleading. Consequently, we exploited the topological feature of $\nabla\rho(r)$; maximum, minimum and saddle points. The saddle points are

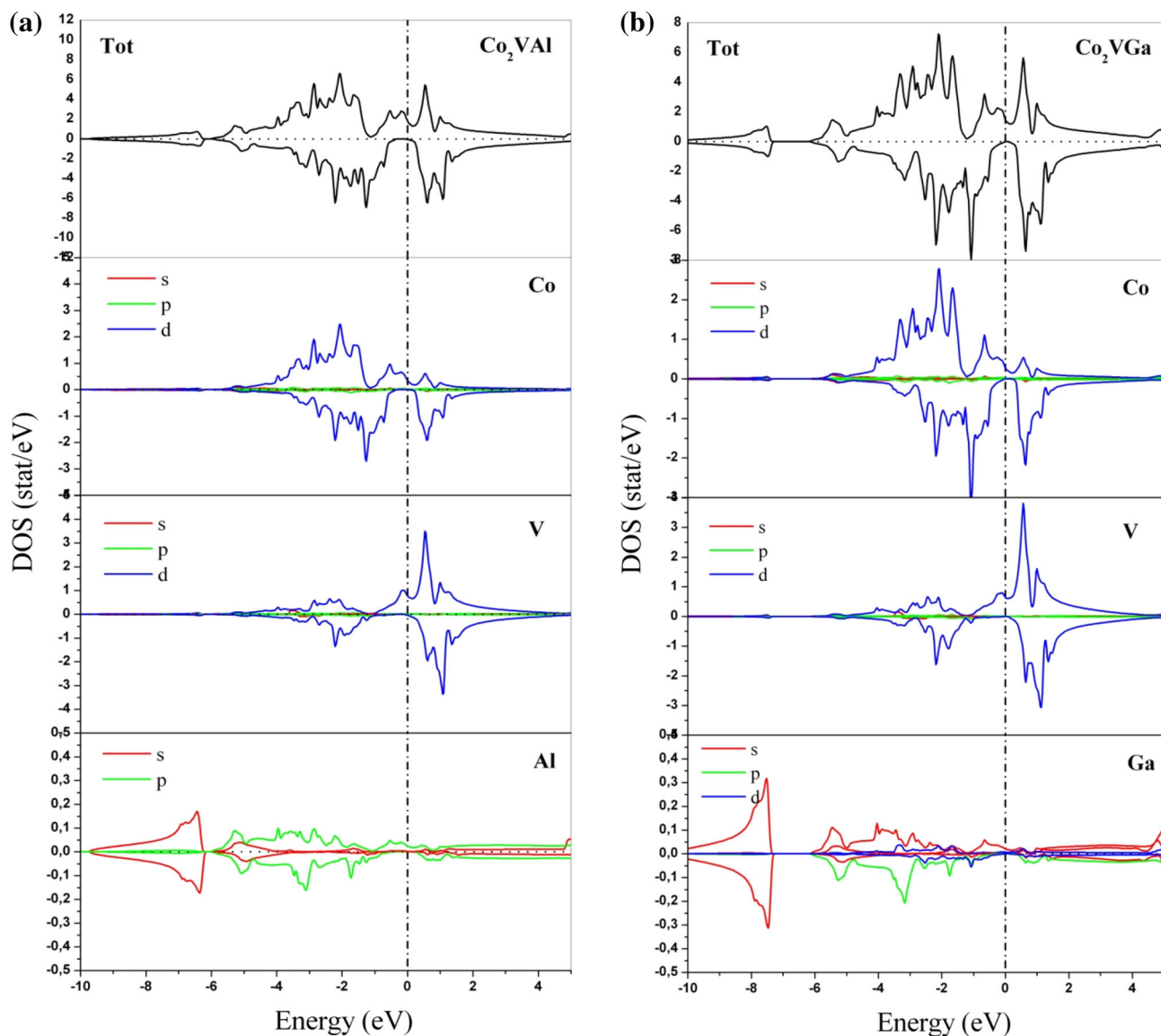


Fig. 4. (a) Calculated spin-projected total and partial DOS plots for the Co_2VAI , and (b) Co_2VGa .

associated with critical points (CP), and denoted by the coordinate r .

The charge density in the neighborhood of a critical point was obtained through an algorithm implemented in the critical code and based on the recursive division of the irreducible wedge of the Wigner–Seitz polyhedron and the minimization of $|\nabla\rho(r)|$ within the edges, surfaces and interiors of the resulting tetrahedral.

Figure 5 shows the most significant and comprehensive form obtained by depicting the attraction basins for each nuclei. The site symmetry has helped to establish the specific positions of the cell

that should be the CPs of the electron density forming an “atomic basin”. Due to the difference of the electro-negativity between the aluminum and gallium atoms, the two compounds under study somehow showed a difference in terms of the topology of their electrons and also the charge transfer between atoms. There is a topological index that has been proposed as a global measurement of the degree of metallicity, namely the electron density *flatness*, which is defined as⁴⁸

$$f = \frac{\rho_c^{\min}}{\rho_b^{\max}} \quad (2)$$

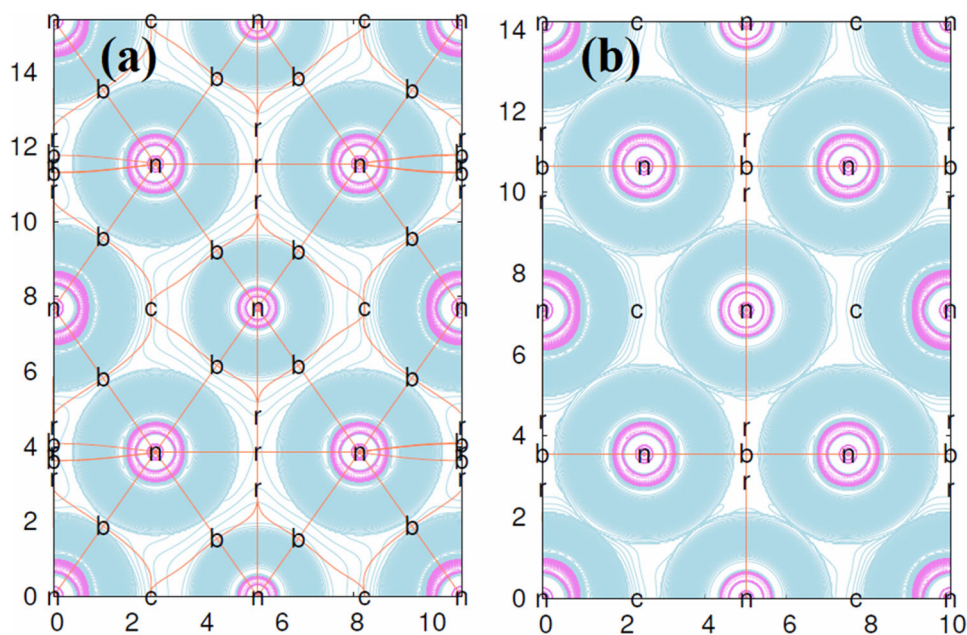


Fig. 5. Electron density in the [100] plane: (a) Co_2VAl and (b) Co_2VGa . This plane contains all the critical points (CPs) of the structure: the three nuclei, the Co-Al/Co-Ga and Co-V bonds CPs, a single ring CPs, and two different cages CPs. The down trajectories from the bonds CPs and the up trajectories from the r CP show the limits of the central ionic basin. Thick red lines correspond to the $\tilde{N}r$ trajectories, magenta lines are positive (negative) contours of r and $\tilde{N}2r$. The scale of this plot are respectively in (electron \times bohr-3) for ($r, \tilde{N}r$) and (electron \times bohr-5) for $\tilde{N}2r$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

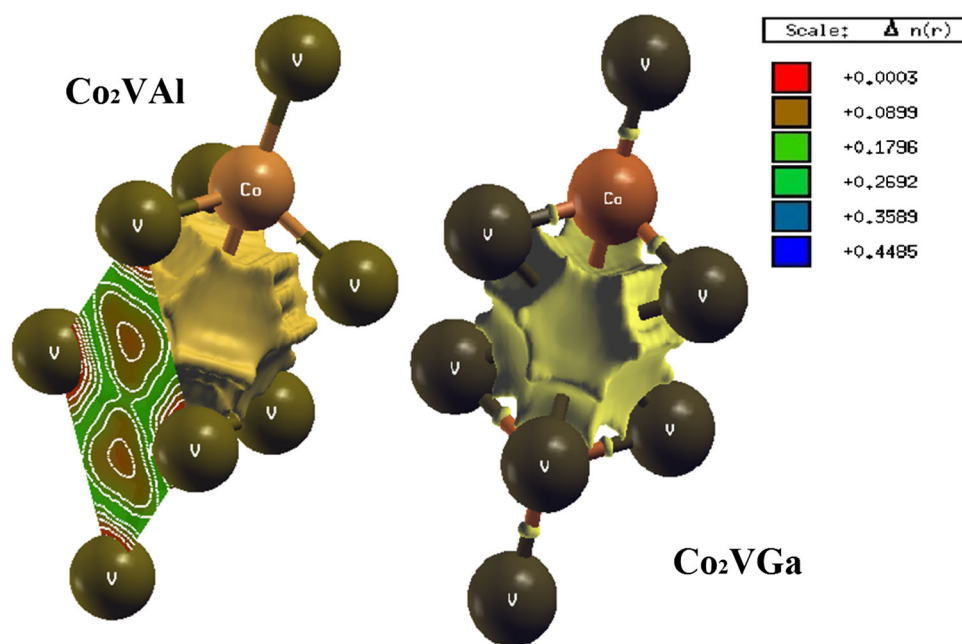


Fig. 6. Three-dimensional (3D) iso-surface plot of the electron localization function for (right) $\text{ELF} = 0.22$ for the Co_2VAl and (left) $\text{ELF} = 0.19$ for the Co_2VGa compounds.

where ρ_c^{\min} is the absolute minimal electron density found on the unit cell (necessarily a cage CP of ρ , and ρ_b^{\max} is the maximal electron density among the

bond CPs). This index separates metals (with f approaching one) from nonmetals (f going to zero) by exploiting the idea that the relevant portion of the

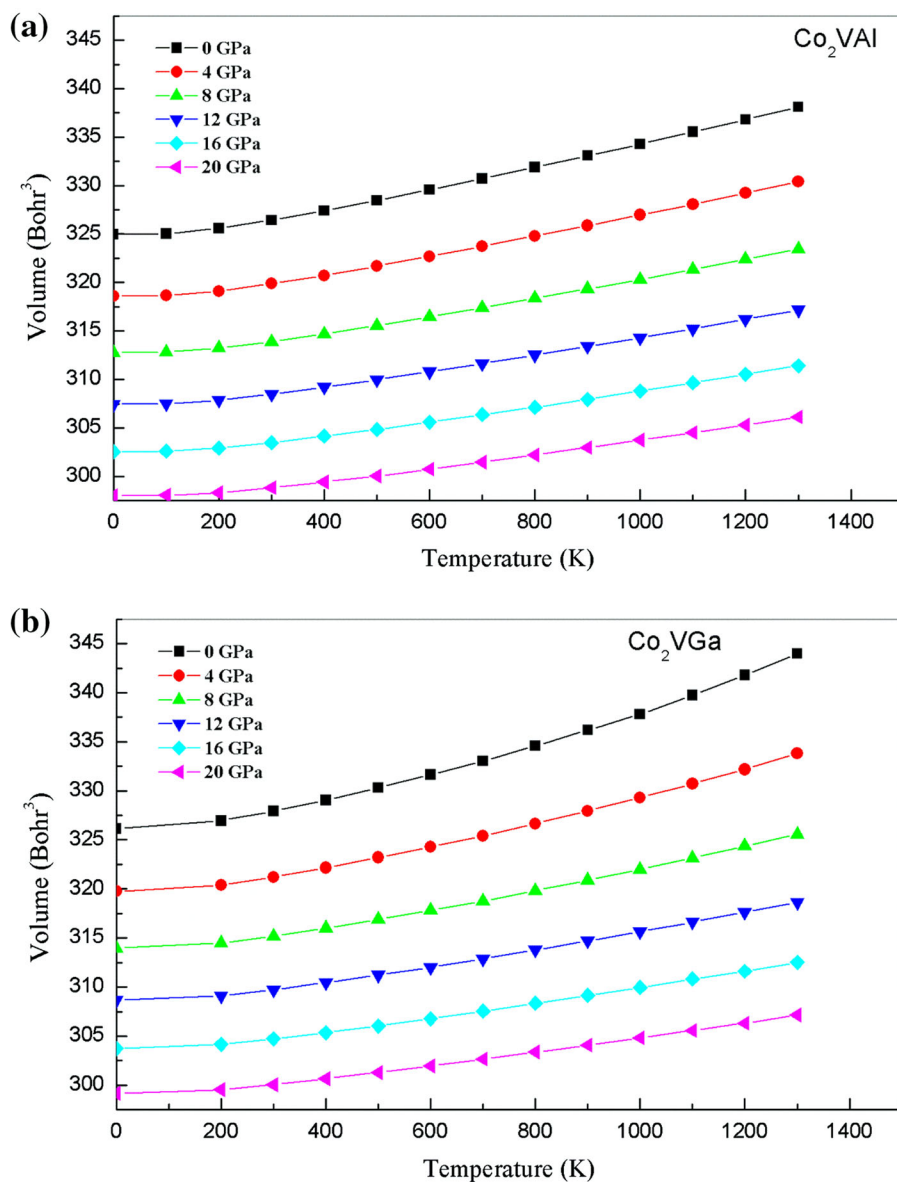


Fig. 7. The temperature effects on the lattice parameter for (a) Co₂VAI (b) and Co₂VGa alloys.

valence electron density starts at the highest density and ends at the lowest density cage CP. Together, c and f have been shown to provide a classification of the crystal topologies into the three ionic-covalent-metallic prototypes⁴⁸ that closely resemble the van Arkel and Ketelaar classical triangle^{49,50} based on electronegativities.

Due to the difference of the electronegativity between Al and Ga atoms, both compounds show a certain difference in their topology and in the charge transfer between atoms. The calculation of

the net charge allowed us to provide a better understanding of the bonding behavior of our compounds. The Co₂VAI compound is 73.45% metallic whereas the Co₂VGa has 96.46% of this bonding compartment. However, as is known from the Pauling concept, the metallic bond is basically a partial covalent bond. We then exploited the ratio of the net charges of an atom in a material and the charges of its nominal oxidation state to calculate the total charge transfer and the ionicity degree. Doing so, the calculated covalent character for the

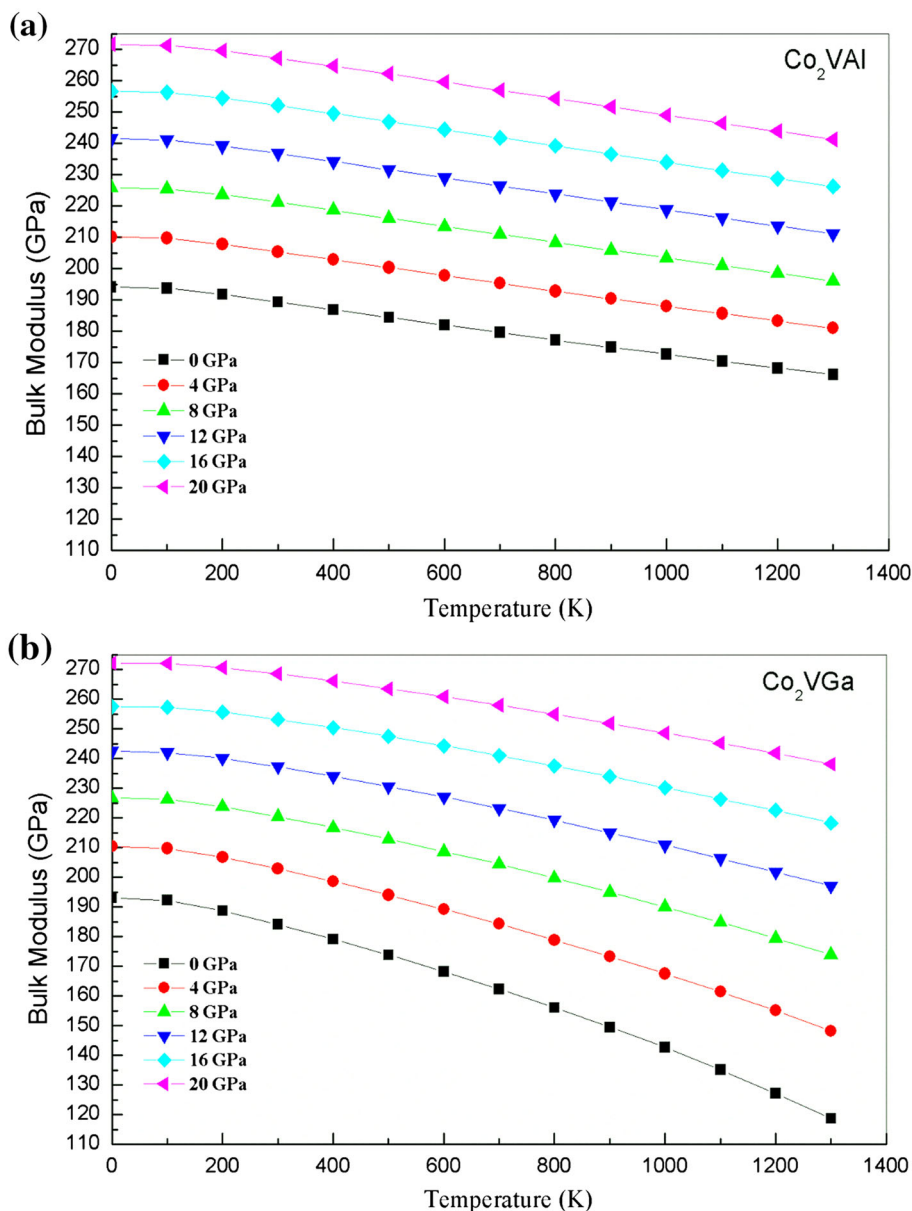


Fig. 8. The temperature effects on the bulk modulus for (a) Co_2VAl (b) and Co_2VGa compounds.

Co_2VAl and Co_2VGa compounds were 61.2% and 83.3%, respectively.

In the Co_2VAl compound, the net charges of the cobalt, vanadium and aluminum atoms are $-1.25807802e$, $+0.89608770e$ and $+1.62288231e$, respectively (where e is being the fundamental charge), whereas in the case of the Co_2VGa compound, the net charges of cobalt, vanadium and gallium atoms are $-0.547e$, $+0.931e$ and $+0.161e$, respectively (the negative values are obviously due to the valence charge related to the electrons).

This prominent chemical bonding features can also be observed by the calculated electron localized function (ELF) isosurface plots,²¹ as displayed in Fig. 6.

The dimensionless ELF magnitude ranges from 0 to 1 with $\text{ELF} = \frac{1}{2}$ corresponding to the free electron gas distribution, $\text{ELF} = 0$ pointing to no localization, and $\text{ELF} = 1$ corresponding to perfect electron localization.

Further evidence of the complete delocalization comes from the representation of the two Heusler

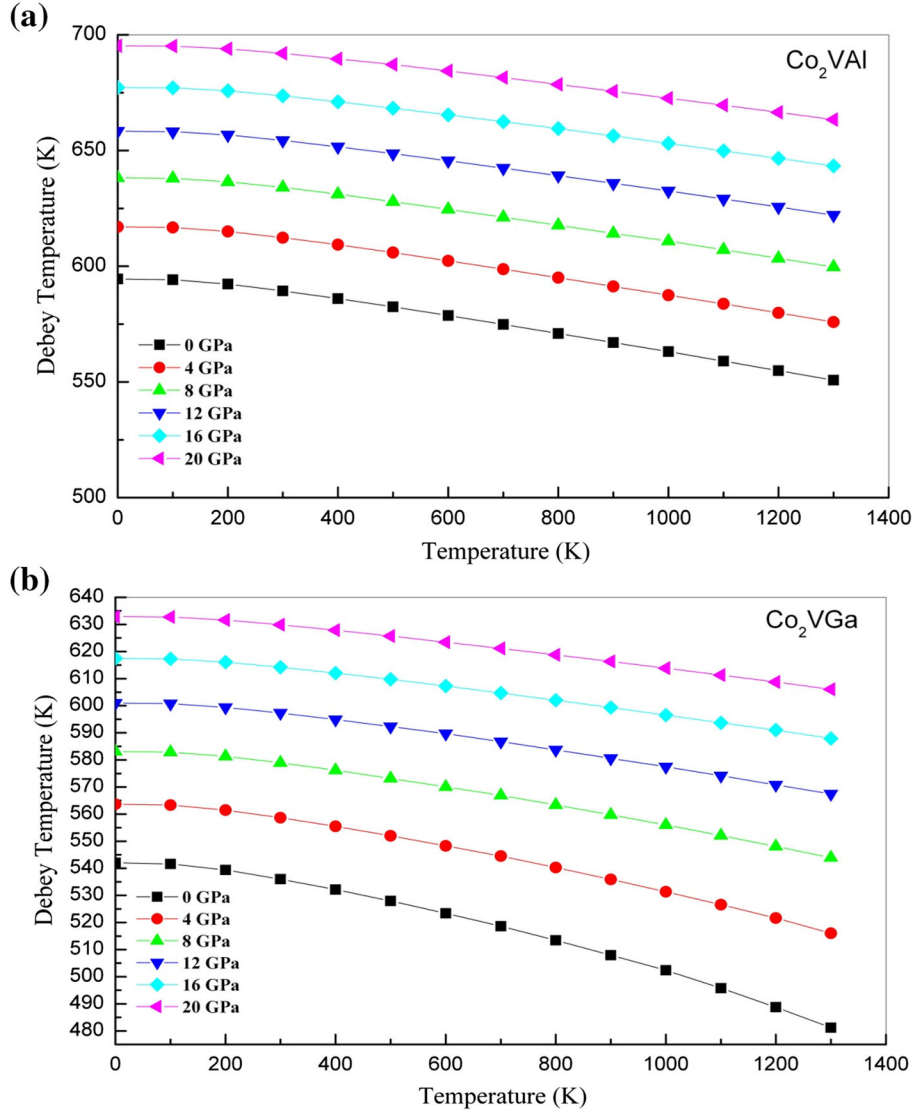


Fig. 9. Variation of the Debye temperature with respect to the temperature at different pressures ranging from 0 to 20 GPa for (a) Co_2VAI (b) and Co_2VGa alloys.

alloys. ELF limit attractors appear for $\text{ELF} = 0.19$ value in the Co_2VGa compound and $\text{ELF} = 0.22$ for Co_2VAI .

Thermal Properties

We applied the quasi-harmonic Debye model⁵¹ to obtain the thermodynamic properties of the Co_2VAI and Co_2VGa compounds through the calculation of the E–V. The first step is to calculate the total energy versus the primitive cell volume (E–V). The obtained results are then fitted with a numerical EOS in order to determine the structural parameters at $P = 0$ GPa and $T = 0$ K.

The macroscopic properties are derived as a function of P and T from the standard thermodynamic relationship. The thermal properties are

determined in the temperature range from 0.0 to 1300 K where the quasi-harmonic model remains fully valid. The pressure effect was studied in the 0 to 20 GPa range.

The variation of the volume with respect to the temperature at different pressures is shown in Fig. 7a and b. The volume was found to increase slightly with increasing temperature. The variation of the bulk modulus B as a function of the temperature at a constant pressure is shown in Fig. 8a and b. The bulk modulus was found to decrease with increasing temperature at a constant pressure and also to increase with pressure at a constant temperature.

In Fig. 9a and b, it can be seen that the impact of the temperature variation on the Debye

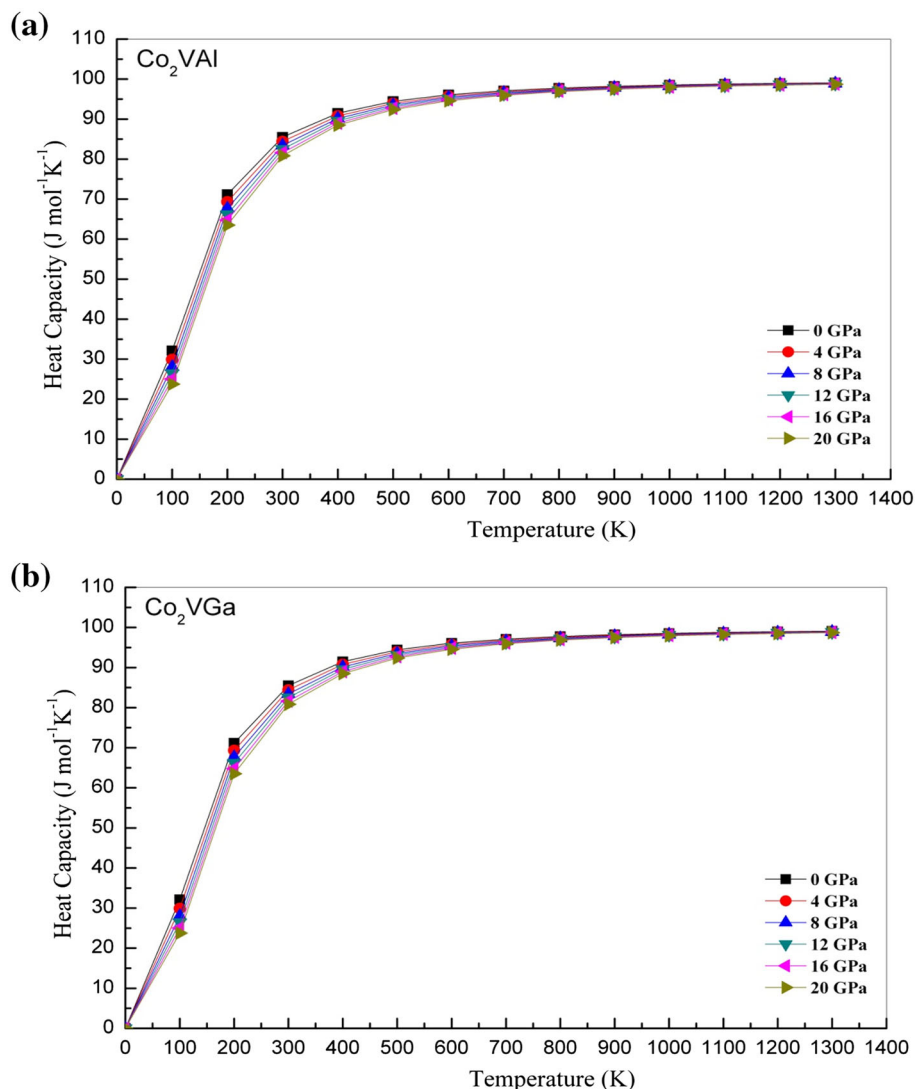


Fig. 10. The heat capacity depending on the temperature for different pressures from 0 to 20 GPa for (a) Co_2VAl (b) and Co_2VGa compounds.

temperature is less than that of the pressure, and also that the decreasing trend is nearly linear for each pressure. These investigations demonstrate clearly that we can classify our compounds among the hard materials category due to their high Debye temperature.

In fact, the Debye temperatures of the full-Heusler alloys Co_2VAl and Co_2VGa at equilibrium are 589.1 K and 535.8 K, respectively.

In addition, relevant information about the lattice vibrations can be obtained by the constant volume heat capacity (C_v). The investigation of C_v as a function of the temperature at different pressures of 0, 4, 8, 12, 16 and 20 GPa is shown in Fig. 10a and b. At high temperatures, C_v tends to the Dulong and Petit limit, which is rather common for all solids.⁵²

At sufficiently low temperatures, C_v is proportional to T^3 ,⁵³ while at equilibrium, the heat capacity for the Co_2VAl and Co_2VGa compounds are found to be $83.24 \text{ J mol}^{-1} \text{ K}^{-1}$ and $85.71 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

Figure 11a and b represents the variation of the thermal expansion coefficient $\alpha(T)$ of the Co_2VAl and Co_2VGa as a function of the temperature and the pressure. It is shown that, at a constant pressure and at low temperatures, α increases with temperature—especially at zero pressure—and gradually tends to a linear increase at higher temperatures. As the pressure increases, the increase of α with the temperature becomes smaller, while at a constant temperature, α decreases strongly with increasing pressure.

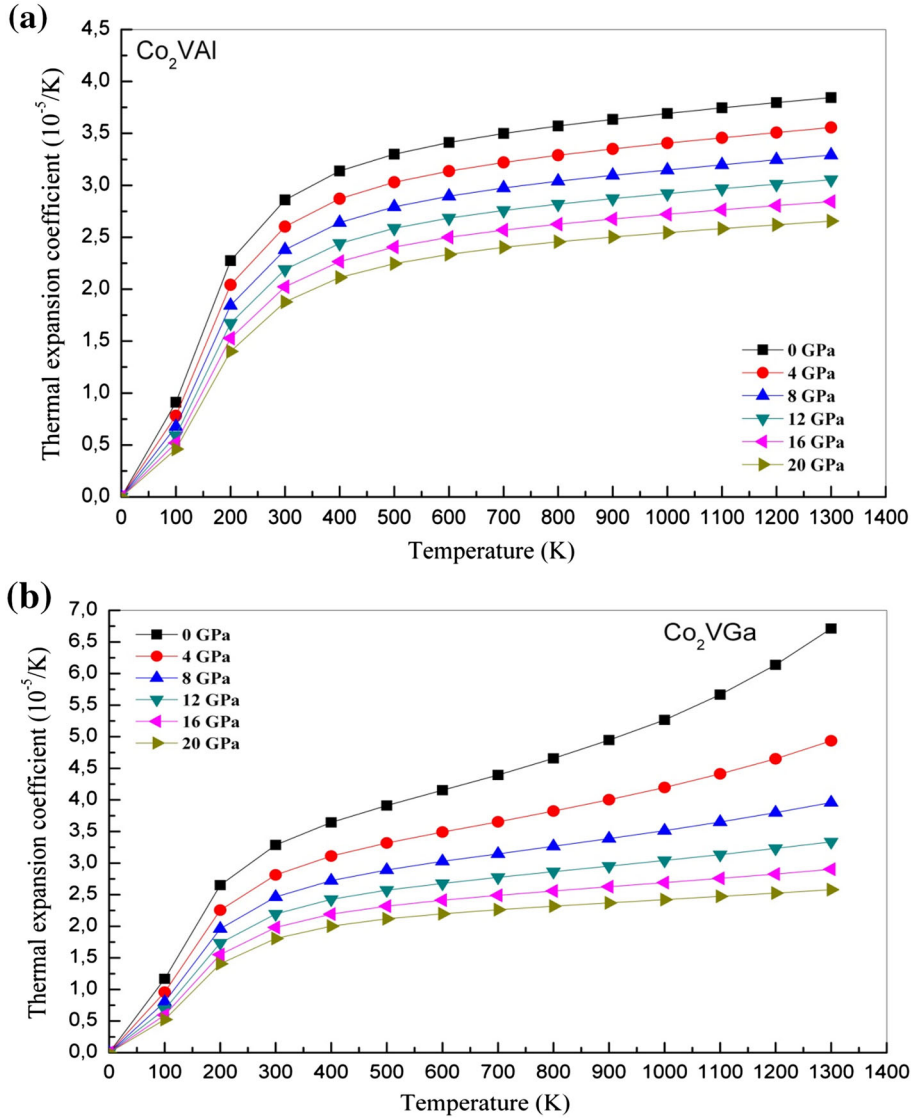


Fig. 11. The thermal expansion coefficient as a function of the temperature at different pressures ranging from 0 to 20 GPa for (a) Co₂VAI (b) and Co₂VGa alloys.

CONCLUSIONS

By using the full-potential linearized augmented plane-wave method within the Perdew–Burke–Ernzerhof generalized-gradient approximation we have investigated the structural, magnetic and thermal properties of the Co₂VAI and Co₂VGa compounds. A reasonable agreement was found between our theoretical results and the available experimental data. We have shown that the d–d hybridization between the transition atoms (Co–Co and Co–V) of these compounds was essential for the formation of the gap at the Fermi energy level. The calculated total magnetic moment for the Co₂VAI and Co₂VGa was found to be equal to 2 μ_B and 2.09 μ_B , respectively. Moreover, in order to analyze in depth the bonding nature of these compounds, the ELF and AIM approaches were used, and thereby confirmed the

nature of the metallic bond. On the basis of the quasi-harmonic Debye model, and in the temperature range from 0.0 K to 1300 K, the thermodynamic properties, including the variation of volume, bulk modulus, heat capacity, thermal expansion and the Debye temperature, were predicted in the whole pressure range from 0.0 to 20.0 GPa. Since there are no experimental data available for these quantities, we believe that our results could serve as a reference for future investigations.

ACKNOWLEDGEMENTS

We acknowledge financial and technical supports from the University Djillali Liabès, at Sidi Bel-Abbes (Algeria), the University of Hassiba Ben Bouali, Chlef (Algeria), would like to acknowledge

the support of the Qatar Energy and Environment Research Institute (QEERI), Hamad Bin Khalifa University, Qatar-Foundation and the institut national de la recherche scientifique –Energie, matériaux et télécommunications, Quebec, Canada. A.H.Reshak would like to acknowledge the CENTEM project, Reg. No. CZ.1.05/2.1.00/03.0088, co-funded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI program and, in the follow-up sustainability stage, supported through CENTEM PLUS (LO1402) by financial means from the Ministry of Education, Youth and Sports under the "National Sustainability Program I. Also MetaCentrum (LM2010005) and CERIT-SC (CZ.1.05/3.2.00/08.0144) infrastructures.

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