

Volume dependence of magnetic properties in $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$ ($Y=\text{Ti-Ni}$) Heusler alloys: a first-principles study

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Abstract

The magnetic properties tuning and volume dependence in the series of quaternary full Heusler alloys with formula $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$ ($Y = \text{Ti, V, Mn, Fe, Co, Ni}$) were studied with a detailed first-principles exploration. We employ the density functional KKR method with the coherent potential approximation, estimating effective Heisenberg exchange constants via the magnetic force theorem together with mean-field Curie temperature (T_C) and magnetic moment for compositions in the whole concentration range. The volumetric dependency of these magnetic properties is studied, particularly the pressure derivatives of T_C at equilibrium. Our ternary alloy calculations show good agreement with local-density and generalized gradient approximations in the literature. The quaternary alloys show a wide range of tunable magnetic properties, where magnetic moments range from 0.8 to $4.9\mu_B$, T_C from 130 K to 1250 K, and dT_C/dV values range from -7 to $+6.3\text{ K}\text{Å}^{-3}$.

Keywords: Heusler alloys, Curie temperature, pressure, volume dependence

1. Introduction

Heusler alloys are known for the great variety of compositions and properties, since many elements can occupy the X , Y and Z sites in the L2_1 structure with fractional occupations [1], allowing a great flexibility. Improved properties may also be obtained by exploring disorder, non-stoichiometric compositions, and variation with external parameters such as magnetic field, temperature and pressure [2]. The exploration of several independent factors can be achieved in a controlled way using first-principles calculations. Interest in Heusler alloys has mainly been concerning electronic structure and transport properties, motivated by application in spintronic devices [3], especially in half-Heusler XYZ and

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full-Heusler Co_2YZ alloys. Other aspects of Heusler alloys have also motivated first-principles studies, including exchange interactions [4, 5], to calculations of the magnetocaloric effect [6, 7] with the aid of Monte Carlo simulations.

In this context, a related aspect which benefits from computation but has been less studied is the variation of exchange interactions, and ferromagnetic Curie temperature (T_C) with volume, or hydrostatic pressure. An initial detailed theoretical study of this subject was concerned with Ni_2MnSn [8]. More recently, $\text{Mn}_2\text{Co}Z$ ($Z = \text{Al, Ga, In, Si, Ge, Sn, Sb}$) compounds have been analyzed [9]. $(\text{Ni}_{1-x}\text{T}_x)_2\text{MnSn}$ ($T = \text{Pd, Cu}$) alloys have also been studied as a function of concentration and pressure [10]. For Cu alloying, a crossover behavior was found, with dT_C/dP changing sign as a function of Cu concentration.

Experimental investigations of T_C with pressure have also been specially focused in the Mn based systems, due to coupling between structure and magnetism (with, e.g. the shape memory and magnetocaloric effects), including $\text{Ni}_2\text{Mn}Z$ ($Z = \text{Al, Ga, In, Sn, and Sb}$) [11, 12], Au_2MnAl and $\text{Pd}_2\text{Mn}Z$ ($Z = \text{Sn and Sb}$) [13]. For all these alloys, wherein Mn has localized moments, the positive dT_C/dP (negative dT_C/dV) measured is consistent with an empirical interaction curve as a function of the distance between Mn atoms [12].

For cobalt-based (Co_2YZ) alloys there have been experiments with $\text{Co}_2\text{TiAl}/\text{Co}_2\text{TiGa}$ [14, 15], Co_2ZrAl [16], and $\text{Co}_2\text{VAl}/\text{Co}_2\text{VGa}$ [17]. These measurements revealed a negative dT_C/dP , which is typical of itinerant magnetism. The $\text{Co}_2\text{Mn}Z$ ($Z = \text{Ga, Si, Ge, Sn}$) alloys, however, display a positive dT_C/dP , in conformity with the other Mn-based systems [18].

In a previous study [19] we have made an investigation of different Co_2YZ compounds, including the variation of lattice parameters, and its effect on magnetic interactions and T_C . In this work we focus in particular on stoichiometries based in the Co_2CrGa compound. Cr is substituted with one of six different elements: Ti, V, Mn, Fe, Co, and Ni, and these alloys are studied with fractional concentrations covering the whole concentration range.

For this kind of system, previous GGA/LDA calculations show good agreement with experimental data. For example, Ref. [20] uses GGA, Ref. [21] is a compilation showing the success of LDA/GGA in Co_2YZ systems, where the moment is well represented as well as T_C (in this case using the random phase approximation). Ref. [22] also shows that the LDA spin moment is consistent with experiment. According to the discussion of Ref. [23], LDA/GGA is sufficient for accurate Curie temperatures (mean field) and magnetic moments, for several Co_2YZ and two $\text{Ni}_2\text{Mn}Z$ alloys, with the only exception for the case of Co_2FeSi (which we do not study here), for which LSDA+U is found to better describe the magnetic moment.

However, with respect to magnetovolume effects, previous calculations have shown significant differences between different exchange-correlation approximations. In *bcc*-Fe, dT_C/dP was found to be -1.4 K/GPa with GGA and -6 K/GPa with LDA [24]. These results are much smaller than previous first-principles results (16 and 18 K/GPa) with a different method [25], and thus the authors claimed a correct prediction of the experimental $dT_C/dP \approx 0$. Nevertheless, these are still significant changes, both relative and absolute. Values of the same

order of magnitude have been found for Heusler alloys (for example, 6.2 and 5.6 K/GPa respectively for Ni_2MnSn and Ni_2MnIn [26]). Therefore, we found it necessary to study the influence of the exchange-correlation approximation in a series of LDA and GGA calculations. We will show that, for the compositions containing Ti and V, dT_C/dV is strongly dependent on the exchange-correlation functional: the measured sign is obtained with the local density approximation, but not with the generalized gradient approximation.

Using the LDA, we find that those compositions close to Co_2TiGa and Co_2VGa display positive (negative) dT_C/dV (dT_C/dP), as measured, and expected for itinerant magnetism. Moving forward in the transition metal period to Cr, Mn, and Fe, dT_C/dV (dT_C/dP) becomes negative (positive), consistent with localized moments.

To our knowledge Co_2NiGa forms in a disordered *fcc* or ordered Pt_2FeCu -type structure [27], while Co_3Ga is not known in any form. We will also analyze the alloying of Co and Ni in the quaternary alloys with the L2_1 structure, bearing in mind that we are not describing known compounds in these cases. A previous first-principles study has already analyzed the stability of Co_2NiGa , and found, as expected, that the ground state cubic structure is metastable with respect to the tetragonal distortion [28]. However, $\text{L2}_1\text{-Co}_2\text{NiGa}$ may be formed with novel synthesis methods, and the fractional alloys with Cr should be synthesized more easily than the ternary compounds, especially for low substitution concentrations. For the compositions close to Co_3Ga and Co_2NiGa our calculations show dT_C/dV (dT_C/dP) again positive (negative). Therefore, substituting Ti, V, Co, or Ni for Cr gradually decreases dT_C/dV and eventually changes its sign.

2. Calculation Details

We use the KKR Green's function density functional theory, as implemented in the SPR-KKR code [29, 30]. The full potential¹ spin-polarized scalar-relativistic method is used. As the exchange-correlation approximation we consider the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof parameterization [31] and the local density approximation (LDA) with the Vosko-Wilk-Nusair parameterization [32] for the ternary compounds. The LDA is used for the detailed study of the alloys. The reciprocal space is sampled with a $22 \times 22 \times 22$ \mathbf{k} -mesh, the calculation in the complex energy path uses 32 points, and the angular momentum cutoff is $l = 3$. The magnetic order is assumed ferromagnetic, which is consistent with the known measured cases, such as the ternary compounds (also under pressure), and with Fe or Mn doping [33, 34]. For the quaternary, fractional alloys, we sample variation of different concentrations of transition metal element substitutions in the *Y* site of the L2_1 structure, with chemical formula $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$, and considering six neighbor elements

¹The use of the full potential by Thoene et al. [23] was found important in some cases to obtain accurate Curie temperatures.

($Y=\text{Ti, V, Mn, Fe, Co, Ni}$). The coherent potential approximation is used to simulate the disorder in that site [35].² Steps of $\Delta x = 0.1$ were considered.

Self-consistent total energy calculations at different volumes are used with the Murnaghan equation of state [37] to fit the energy-volume curve and find the corresponding pressures. (There are no internal relaxations involved due to the symmetries of the $L2_1$ structure.)

The exchange constants of an effective Heisenberg model are calculated with the magnetic force theorem of Liechtenstein et al. [38]. For this calculation a cluster of radius four times larger than the $L2_1$ cell lattice constant is considered around each site and all the pairwise interactions in that cluster are calculated, considering the four sublattices. T_C is determined in the mean field approximation for a multisublattice system [39, 8], i.e., using the highest eigenvalue of the matrix \mathbf{J} containing the pairwise exchange interaction sums.

3. Results

3.1. Ternary compounds: exchange-correlation approximation and comparison with experiments

The calculated lattice parameters and magnetic moments are shown and compared with experiments [17, 22, 33, 40, 41] in Table 1. GGA is more accurate for the lattice parameters. The bulk moduli are also shown, and follow the usual tendency of larger values for LDA, with smaller lattice parameters. With regards to the magnetic moments, there is not one approximation consistently better for all compounds: LDA is better for Co_2TiGa , GGA is better for Co_2FeGa and slightly better for Co_2CrGa , while for the other compounds both approximations have similar accuracies. For all compositions except Co_2CrGa , the T_C obtained with LDA is closer to the experimental [40, 42, 43, 44, 33] one than that obtained with GGA. This does not necessarily mean that LDA produces a better estimate of the exchange constant values than GGA, since the mean field approach used here usually overestimates T_C .

Although the mean field approach to Curie temperatures usually overestimates Curie temperatures, Thoene et al. [23] have obtained T_C close to the experimental values for a variety of Heusler compounds. For the case of Co_2CrGa , it was even underestimated, 366 K with respect to the experimental value of 495 K [43]. However, this comes from using the experimental lattice parameters instead of the theoretical ones. As shown in Tab. 1, the T_C calculated at the theoretical LDA lattice is close to the experimental one. We also find similar values of the derivatives dT_C/dV with both approximations at the equilibrium values.

For other compositions, dT_C/dV does not always show such a good agreement between functionals. This is shown here for Co_2TiGa , Co_2VGa , Co_2MnGa ,

²It was previously shown [36], by comparison with supercell calculations, that short-range interactions should not affect the magnetic properties significantly for the type of alloys we are considering.

Table 1: Comparison of the calculated (GGA and LDA) equilibrium lattice parameters a_0 (Å), bulk moduli B (GPa), Curie temperature T_C (K), magnetic moment m (μ_B), dm/dV ($10^{-3} \mu_B \text{Å}^{-3}$), and dT_C/dV (KÅ^{-3}) at the equilibrium lattice parameters, and experimental T_C and a_0 .

Compound	GGA						LDA						exp.		
	a_0	B	T_C	m	dT_C/dV	dm/dV	a_0	B	T_C	m	dT_C/dV	dm/dV	a_0	T_C	m
Co ₂ TiGa	5.87	179	243	0.97	-1.2	-0.2	5.72	216	130	0.82	4.5	5.1	5.86	128	0.82
Co ₂ VGa	5.80	194	469	1.96	-1.5	-2.8	5.66	237	345	1.96	1.7	-1.2	5.78	352	2.04
Co ₂ CrGa	5.75	195	485	2.99	-5.3	9.9	5.61	247	470	2.96	-4.6	0.4	5.81	495	3.01
Co ₂ MnGa	5.75	187	662	4.09	-8.2	13.8	5.60	237	670	4.01	-7.0	9.2	5.77	685	4.05
Co ₂ FeGa	5.75	187	1317	4.99	-4.9	17.4	5.60	231	1252	4.87	-3.2	26.5	5.74	1093	5.15

and Co_2FeGa . For Co_2MnGa and Co_2FeGa , similarly to Co_2CrGa , there are quantitative differences but the results are still consistent, since the derivatives are not far in the two cases and have the same sign. For Co_2VGa , however, the T_C dependence changes sign with the different approximations, at the theoretical lattice parameters. The difference of the derivative between approximations is not far from the other cases, but some factors contribute to the change of sign: small values near the theoretical parameters, and the large variation of the value with volume in LDA, plus the usual overbinding of LDA. For Co_2TiGa , the volume dependence of the Curie temperature is even more distinct for the two functionals, an almost constant behavior with negative slope with GGA, but a steeper, positive dependence with LDA. (Note: dT_C/dV values were calculated with respect to the $L2_1$ unit cell volume differences. If we used the volume per formula unit, the values would be four times larger.)

It is also interesting to analyze the change of the magnetic moments with volume. For $Y=\text{Mn}$ and Fe the results are consistent for both approximations only with small quantitative differences, as in dT_C/dV , but with opposite sign. For the case of Co_2TiGa we have exactly the same sign change as in dT_C/dV , indicating the change of m as the main factor in the variation of the exchange interactions. In contrast, for Co_2VGa dm/dV has the same sign between functionals, opposing the dT_C/dV behavior. For Co_2CrGa , dm/dV is much higher for GGA than for LDA (where it is almost zero since m is a minimum close to equilibrium). This also contrasts with the T_C dependence, which is basically the same, negative and not insignificant, for both functionals.

The T_C values and its variation with volume and approximation (LDA/GGA) can be explained as a result of the underlying exchange interactions. The two largest exchange interactions are shown in Table 2. For Co_2FeGa and Co_2MnGa , $J_{\text{Co}-Y}$ is much larger than the next largest interaction, Co-Co, and both interactions decrease with volume, consistent with T_C . $J_{\text{Co}-\text{Fe}}$ decreases slightly faster for GGA, as with T_C . For Co_2CrGa , $J_{\text{Co}-\text{Cr}}$ is only slightly larger than the Co-Co interaction. The dependence of the first interaction is slightly steeper for LDA, consistent with the small quantitative difference between approximations. Co_2VGa and Co_2TiGa are different, since here the first Co-Co is much larger than the first Co- Y interaction, which is already insignificant. For Co_2VGa the first Co-Co interaction has the same variation in both approximations, although with GGA the variation is less steep, and it is not enough to account for the sign change with dT_C/dV (it must be accounted by considering Co-Co at larger distances, which also have distinct volume changes between LDA and GGA). For Co_2TiGa the first two Co-Co interactions show the same behavior as T_C . The distinct behaviors between functionals for $Y=\text{Ti}$, V can then be ascribed to the different descriptions of Co-Co interactions.

Table 3 summarizes present experimental knowledge of dT_C/dP in our alloys, including Co_2TiGa and Co_2VGa , along with our results. The sign is correct, but only if we consider the LDA calculations, as the GGA calculations give the opposite sign. Even considering the LDA results, the calculated values are ~ 3 and ~ 5 times smaller for Co_2TiGa and Co_2VGa , respectively.

The main reason for this disagreement is unclear at present. Alling et al.

Table 2: Two largest pairwise exchange interactions (meV) for the ternary compounds Co_2YGa ($Y=\text{Ti, V, Cr, Mn, Fe}$), calculated with LDA and GGA (in parenthesis). J^1 is $J_{\text{Co}-\text{Y}}$ for $Y=\text{Cr, Mn, Fe}$, and $J_{\text{Co}-\text{Co}}$ for $Y=\text{Ti, V}$.

Compound	J^1	$J_{\text{Co}-\text{Co}}^2$
Co_2TiGa	2.56 (4.59)	1.26 (2.35)
Co_2VGa	6.74 (8.29)	1.54 (2.17)
Co_2CrGa	4.55 (5.88)	3.72 (4.35)
Co_2MnGa	10.62 (11.50)	1.49 (1.92)
Co_2FeGa	21.75 (22.62)	2.30 (2.56)

Table 3: Comparison of the measured and calculated (LDA and GGA) dT_C/dP (K/GPa) in Co_2VGa and Co_2TiGa .

Compound	Measured	LDA	GGA
Co_2TiGa	-13 [14]; -12.7 [40]	-4.0	+0.4
Co_2VGa	-7.8 [17]	-1.5	+1.2

have suggested that to improve T_C estimates it should be necessary to consider also finite-temperature effects, such as magnetic excitations and chemical disorder [45]. In that work, it was also shown that the use of the disordered local moment state as the reference for the calculation of exchange interactions may bring some change in the dependence of T_C with volume. For Ni_2MnSn [8], the calculated value 3.22 was also smaller than the experimental 7.44 (K/GPa), and it was calculated that intersublattice interchange between Mn and Ni can strongly increase dT_C/dP . A similar antisite disorder may affect the samples discussed here. Theoretical improvements may also play a role, such as more sophisticated Curie temperature calculation approaches (such as the random phase approximation) and, as we have shown here, different exchange-correlation functionals.

We will continue with a detailed study of the fractional alloys using LDA, due to its better agreement with experiment for dT_C/dP .

3.2. Quaternary alloys

Fig. 1 shows the optimized lattice parameters for all the compositions studied. The variation of the lattice parameter with the concentration of the transition metal is approximately linear.

In what follows we will consider the magnetic properties, in order of atomic number for the six neighbor elements of Cr which we considered in our calculations.

Figs. 2(a) and 2(b) show the magnetic spin moments for small volume variations (lattice parameter with $\pm 1\%$) around the theoretical equilibrium values. The approximate linear variations as a function of the valence electron concentration are in line with a generalized Slater-Pauling rule (also observed in many other Co-based full-Heusler compounds [46]) with the slight deviations for the Ti and Fe rich compositions showing respectively slopes $dM/dn_{el} > 1$

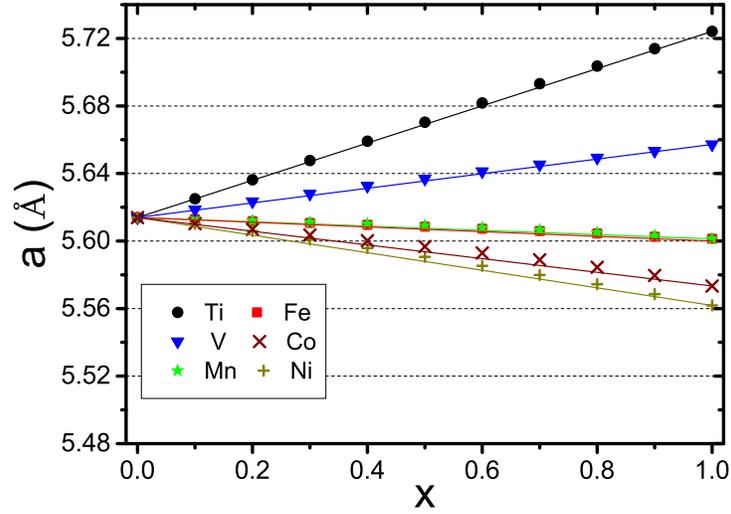


Figure 1: Theoretical lattice parameters for different compositions $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$ ($Y=\text{Ti}, \text{V}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). The lines connect the endpoints. (The Mn and Fe points are superposed in the graph, showing almost the same values.)

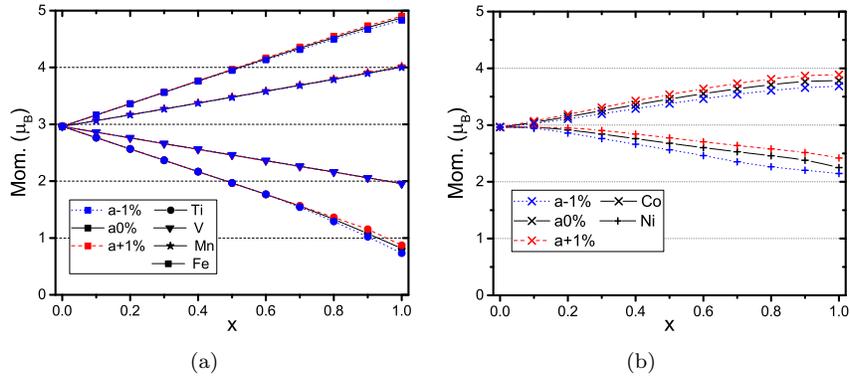


Figure 2: Magnetic spin moments (μ_B) for the alloys $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$ ($Y = \text{Ti}, \text{V}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$), as a function of the concentration x for different calculated lattice parameters around the equilibrium values.

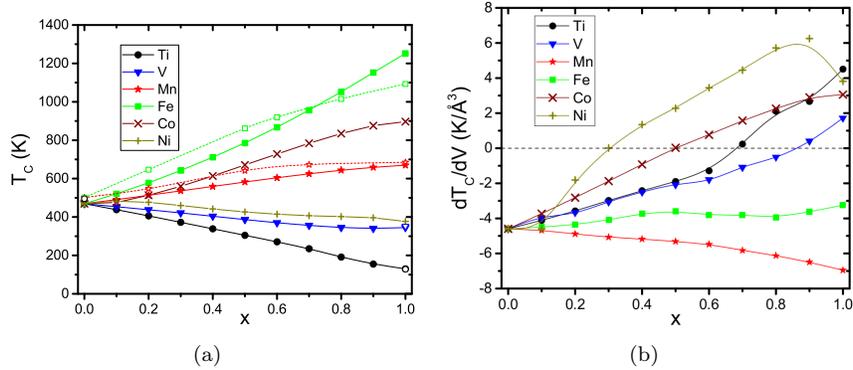


Figure 3: a) Curie temperature (K) for the alloys $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$ ($Y=\text{Ti, V, Mn, Fe, Co, Ni}$) at the equilibrium lattice parameters, as a function of the element concentration. The open symbols correspond to experimental values. b) corresponding derivative of the Curie temperature with respect to volume ($\text{K}\text{\AA}^{-3}$). The lines are guides to the eye.

and $dM/dn_{el} < 1$, resulting in moments slightly less than $1\mu_B$ and $5\mu_B$ respectively. Alloying with Ti strongly reduces the spin moment. Co_2TiGa has a moment close to $0.8\mu_B$ at the theoretical lattice parameter, and we have further calculated that with smaller lattice parameters the magnetic moment falls quickly (not shown) and at a critical pressure of about 30 GPa it vanishes.

For compounds close to the Cr and V rich compositions the magnetic moment is insensitive (changing less than $0.01\mu_B$) to the volume changes considered ($\pm 1\%$ in the lattice parameter). It is also almost insensitive (changing $0.02\mu_B$) for Mn rich compositions. For Fe rich compositions it becomes slightly sensitive ($0.07\mu_B$). For high concentrations of Ti and even at low concentrations of the other transition metals (Co, Ni) the spin moments become significantly (more than $0.1\mu_B$) dependent on volume. The spin moment with full Co substitution is close to $4\mu_B$, consistent with the decrease of moment with electrons after Fe ($\approx 5\mu_B$), following the rule $M = 34 - Z$ for itinerant metals [47]. Co_2NiGa follows the same decreasing trend, but reaches a lower value than expected, closer to $2\mu_B$ than $3\mu_B$.

In all cases, at a given composition the dependence is such that higher volumes always lead to higher moments. The variation of spin moments with lattice parameters is usually negligible when compared with the changes that can be achieved with changing composition. However, this is not so in the compositions close to Co_2TiGa , where a relatively small pressure can decrease the moments significantly, and for compositions close to the Co_3Ga and Co_2NiGa cases, where a change in the lattice parameter of 1% can produce moment changes of $0.15\mu_B$, comparable to a change of $x = 0.3$ in composition.

The calculated Curie temperatures at the equilibrium lattice parameters are shown in Fig. 3(a). dT_C/dV is shown in Fig. 3(b), also for the equilibrium lattice parameters. For the Ti case it shows negative values on the Cr rich side and

positive values on the Ti rich side. At $x_{\text{Ti}} \approx 0.6$ (where T_C is close to 300 K), dT_C/dV is very small. With V substitution T_C also falls, and similarly dT_C/dV also changes sign, in this case at V rich compositions ($dT_C/dV \approx 0$ at $x \approx 0.8$). With V doping, it is possible to get T_C close to room temperature (~ 350 K) at high vanadium concentrations, and with compression it is possible to further reduce T_C . With Mn doping dT_C/dV becomes more negative. In spite of the great range of Curie temperatures for Fe alloying, the respective change with volume is the most constant in all the substitutions. With Co, T_C increases from 450 to 900 K. Just as with Ti and V, dT_C/dV changes sign from negative to positive, and at $x_{\text{Co}} \approx 0.5$, $dT_C/dV \approx 0$. With Ni T_C changes little, while dT_C/dV changes from negative to positive with increasing Ni concentration, reaching the highest values for Ni-rich compositions.

T_C varies monotonically with concentration x of the elements, with no anomalies between the extremes, except where the minimum T_C is achieved slightly away from full V substitution, and a local T_C maximum for low Ni concentrations. dT_C/dV usually also presents extremes at the endpoints, except for Fe and Ni substitutions. In the case of Fe the derivative is not monotonic, nevertheless varying little, in the interval $[-4.4, -3.2]$ K \AA^{-3} . For Ni the maximum and minimum derivatives are reached slightly away from the endpoints.

For the cases of Fe and Mn doping there are previous experimental measurements and calculations, showing a progressive and large increase of the Curie temperature [33, 34], consistent with our results, although there are differences in the values and curvature of the $T_C(x)$ dependence. For the end compounds there are also measurements of T_C [33, 40, 41, 44], and we find very good agreement with our results, except for Co_2FeGa , where the calculated value is higher.

The suppression of magnetism with pressure in the (Ti,V) compounds is concomitant with a high positive dT_C/dV , with the largest value achieved for Co_2TiGa , which is nevertheless smaller in magnitude than the opposite sign value -7 achieved in Co_2MnGa . However, the (Ti,V) compounds present values of T_C closer to room temperature, which may be useful for devices, with applications in room temperature refrigeration or spintronics, for example. Finally, we also predict that $\text{Co}_2\text{Cr}_{1-x}\text{Ni}_x\text{Ga}$ alloys present high values of $dT_C/dV \approx 6$ near the rich Ni side, if these composition are synthesized in the L2_1 structure, while Co rich compositions reach values close to Co_2TiGa .

4. Conclusions

We studied magnetic and magnetovolume coupling properties of fractional $\text{Co}_2\text{Cr}_{1-x}\text{Y}_x\text{Ga}$ alloys ($Y=\text{Ti, V, Mn, Fe, Co, and Ni}$). The equilibrium lattice parameters follow approximate linear variations with changing element concentrations, as well as the magnetic moment (in line with the generalized Slater-Pauling rule, due to the addition/subtraction of valence electrons) except for $Y=\text{Co}$ and Ni. Ti, V, Co and Ni substitutions change the sign of dT_C/dV with respect to the parent Co_2CrGa compound. However, at least for the Ti and V cases the values are dependent of the exchange-correlation approximation, and

the measured sign is only found with the LDA, which is related to the different descriptions of Co-Co exchange interactions.

The wide T_C range of the studied compositions (100 – 1300 K) and range of magnetovolume couplings (dT_C/dV from -7 to $+6 \text{ V \AA}^{-3}$) establishes the rich behavior of this compound family. Optimization with other elements or different substitutions, disorder and volume optimization may be performed to find alloys with optimized T_C and dT_C/dV values for specific applications (for example, the magnetocaloric effect benefits from a high $|dT_C/dV|$ [48]). Further experimental work would be valuable to compare with theory and study the effects the various approximations on dT_C/dV , which was shown to be very sensitive to the theoretical approach employed.

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