

Article

The Effect of Cr Substitution on the Anomalous Hall Effect of $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ ($x = 0, 1, 2, 3$) Heusler Compounds: An Ab Initio Study

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Featured Application: Our theoretical studies report the anomalous and spin Hall conductivities of $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds in the $L2_1$ crystal structure.

Abstract: Based on density functional theory, we studied the electronic, magnetic, and mechanical properties of $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ ($x = 0, 1, 2, 3$) Heusler compounds with the generalized gradient approximation (GGA) for the exchange-correlation potential. In this study, we report two principal spin-related phenomena, namely, the anomalous Hall effect and current spin polarization of the $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds in the $L2_1$ crystal structure. Heusler compounds, both ideally and inversely ordered, were considered. We found that the calculated magnetic moment of $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ decreased with an increase in the Cr concentration for both ideally and inversely ordered structures, except for Cr_3Al . We also found that the spin polarization for all $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ was larger than 50%, except for Cr_2CoAl in the inverse structure. All the considered Heusler compounds were mechanically stable except for the regular Cr_2CoAl . The Hall current spin polarization was also calculated. We found that Co_2CrAl in the XA structure had the largest spin Hall conductivity of 370 ($\hbar S/e$ cm), and the spin polarization of the induced Hall current was high.

Keywords: first-principles calculation; anomalous Hall conductivity; spin Hall conductivity



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1. Introduction

Spin electronics has recently become an interesting research area because of the exciting promise of spintronic devices revealed to date [1–4]. Materials that can provide a high or pure spin-polarized current are a key ingredient for developing useful spintronic devices. Among magnetic conductors, half-metallic (HM) ferromagnets are one of the most suitable choices. Half-metallic materials are substances that have both metallic and insulating properties. It is fascinating that at Fermi energy, metallic behavior holds for one spin channel, but insulating behavior holds for the other channel. The coexistence of metallic and insulating properties makes these HM ferromagnets particularly attractive. The electronic density of states at the Fermi level is completely spin-polarized, and, thus, in principle, they can provide 100% spin currents. These HM materials can be used for spin filters, spin injection or magnetoresistive devices. Furthermore, some Heusler compounds are also predicted to become half-metals at room temperature as their Curie temperature is high, greater than room temperature. Typically, Heusler compounds are categorized into half- and full-Heusler alloys depending on their crystalline structures. The chemical formula and

crystal structure for half-Heusler compounds are XYZ and $C1_b$, respectively. The chemical formula and crystal structure for full-Heusler compounds are X_2YZ and $L2_1$, respectively. The X and Y atoms are transition metals, while the Z atoms are the main group elements. The original discovery of Heusler compounds occurred with the unveiling of ferromagnetic Cu_2MnAl by Heusler in 1903. Since then, Heusler compounds have been investigated for various purposes. The $NiMnSb$ half-Heusler compound with half-metallicity was presented in 1983 [1], and afterward, intensive research on the half-metallic materials was conducted. To date, a large number of materials with half-metallicity have theoretically been predicted [5] or verified experimentally, such as CrO_2 [6,7]. For example, previous studies on Fe_2YSi ($Y = Cr, Mn, Fe, Co$ and Ni), Ti_2YAl , and $Ti_2Y'Ga$ ($Y = Co, Fe$; $Y' = Cr, Fe$) reported theoretical or experimental half-metals [8–11].

Our previous theoretical studies on full-Heusler alloys showed that most Co-based full-Heusler compounds [12] in the ideal cubic $L2_1$ structure are ferromagnetic and their magnetic moments are significantly large. For example, the spin magnetic moments for Co_2CrAl , Co_2CrSi , Co_2CrGa and Co_2CrGe were 2.998, 3.997, 3.051 and 3.997 μ_B , respectively. Furthermore, Co_2CrAl , Co_2CrSi and Co_2CrGe were theoretically predicted to be half-metallic [12]. Accordingly, the electronic band structure and magnetic properties of full-Heusler compounds were intensively investigated both theoretically and experimentally [13] in previous decades. It was found that the total magnetic moments of these Heusler compounds follow Slater–Pauling-type behavior, where the total spin magnetic moments for these Heusler compounds follow a simple rule that relates to the total valence electrons of the Heusler compounds, i.e., $M_t = N_e - 24$.

Let us describe the Heusler structure together with the regular and inverse structures. The ideal X_2YZ full-Heusler alloy is a cubic $L2_1$ structure with point group 225 ($Fm\bar{3}m$ symmetric; see Figure 1). It consists of four interpenetrating *fcc* lattices with two X atoms placed on A(0, 0, 0) and B($1/2, 1/2, 1/2$), a Y atom on C($1/4, 1/4, 1/4$) and a Z atom on D($3/4, 3/4, 3/4$). The two X atoms are environmentally equivalent in the conventional cell, as shown in Figure 1a. In regular full-Heusler compounds, the atomic arrangement is X-Y-X-Z along the diagonal direction of the cubic cell. In this manuscript, we denote this X-Y-X-Z atomic order as the regular structure. Another so-called inverse-Heusler structure, also known as the XA structure, is where there are more valence electrons in the Y atom than the corresponding X atom. Moreover, the atomic position of B is swapped with C, and, thus, the atomic arrangement is X-X-Y-Z along the diagonal direction of the cubic cell, as shown in Figure 1b. The detailed atomic positions for the regular and XA Heusler compounds in the conventional unit cell are shown in Figure 1.

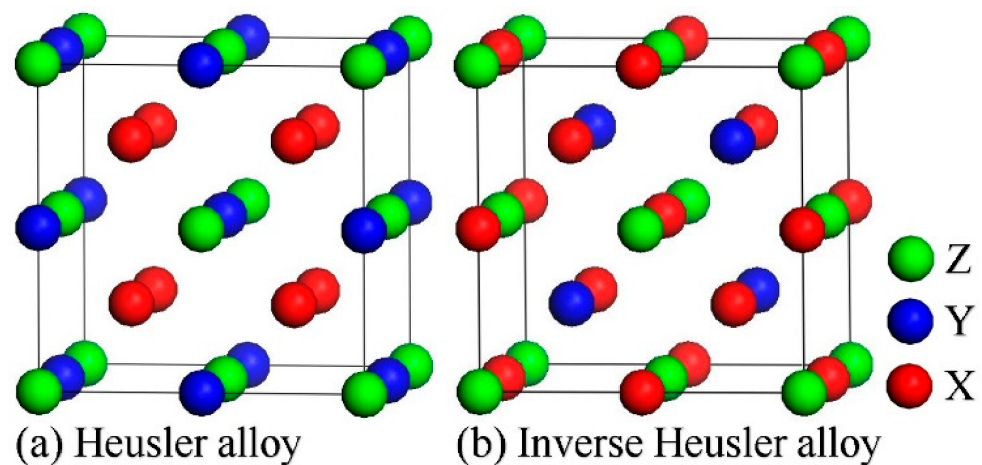


Figure 1. $L2_1$ crystal structure for the (a) regular, and (b) inverse, (XA) Heusler alloys. These are $L2_1$ crystal structures where the atomic arrangement along the diagonal direction differs.

The anomalous Hall effect (AHE) was discovered by Hall in 1881. It describes the anomaly spin-related transport phenomenon in magnetic conductors. It has recently received much attention both in experimental and theoretical studies. In half-metallic ferromagnets, electrons with different spin orientations have completely different conduction behaviors. Therefore, these HMs represent very promising materials for spin-dependent devices. Nonetheless, first-principles investigations of the AHE, especially in half-metallic ferromagnetics, have been few. Discussion of the spin polarization of the transverse Hall current induced by the Hall effect is even more sparse. In this paper, we study the anomalous Hall effect (AHE) and spin polarization of the Hall current in Co-based full-Heusler compounds $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ ($x = 0, 1, 2, 3$) by ab initio calculations of intrinsic anomalous and spin Hall conductivities. Our study focuses on the magnetic properties related to Cr, as well as the regular and XA structures from Co_3Al to Cr_3Al . The results may assist with an experimental search for Heusler compounds with a large AHE, for applications such as magnetization sensors.

2. Theory and Computational Methods

To calculate the intrinsic anomalous and spin Hall conductivities of a solid, we applied Kubo formalism. Following our previous studies [12], we can assert that the intrinsic Hall effect comes from the static limit ($\omega = 0$) of the off-diagonal elements of the optical conductivity. We note that the anomalous Hall conductivity (AHC) calculated in this way is in good agreement with that calculated directly by accounting for the Berry phase correction to the group velocity. We first computed the imaginary part of the off-diagonal elements of the optical conductivity. Then, we obtained the real part of the off-diagonal elements from the corresponding imaginary part using Kramers–Kronig transformation. The intrinsic Hall conductivity σ_{xy}^H is the static limit of the off-diagonal element of the optical conductivity $\sigma_{xy}^{(1)}$ ($\omega = 0$) (see [12] for more details).

The intrinsic Hall effects are driven by spin-orbit coupling (SOC), while the extrinsic Hall effects may be caused by the scattering of magnetic impurities, also known as skew-scattering or a side-jump contribution. For readers who are interested in this research field, Nagaosa et al. published a review article in Reviews of Modern Physics in 2010 [14]. Our first-principles calculations were based on fully relativistic band theory. The SOC effect was included in our theoretical calculations. We calculated the relativistic band structure of the $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds using the projector augmented wave (PAW) method, as implemented in the Vienna ab initio simulation package (VASP) [15,16]. The self-consistent electronic band structure calculations were based on density functional theory (DFT). Generalized gradient approximation (GGA) was applied to describe the exchange-correlation potential [17,18]. We considered the fully ordered cubic Heusler compound structure ($L2_1$). The so-called regular and inversed (XA) Heusler structures differ by the arrangement of the X, Y and Z elements of the Heusler compounds. We will describe those differences later. The cut-off kinetic energy was set to 350 eV. To obtain an accurate ground state charge density, a very fine k-mesh grid of $30 \times 30 \times 30$ was used. The self-consistent cycles were terminated when the total energy differences were less than 10^{-6} eV. To obtain accurate AHC and SHC, a dense k -point mesh is required. We used several k -point meshes to extrapolate the AHC and SHC results in the infinite k -point mesh. To achieve this, we calculated the AHC and SHC as a function of the number of the k points (N_k) in the first Brillouin zone. The theoretical AHC and SHC results were fitted to a polynomial at $N_k = \infty$.

In our theoretical calculations, the charge densities were obtained using $30 \times 30 \times 30$ k-mesh, which is far from sufficient to calculate the anomalous Hall and spin Hall conductivities. Alternatively, there is another method that can theoretically calculate the anomalous Hall conductivity, which is widely used by other research groups. The anomalous Hall conductivities are obtained by making use of the Berry connection. In principle, an infinite number of k points is also needed. This method typically makes use of Wannier interpolation [19], and, thus, a very high k mesh can be used. Our studies

also relied on dense k points; however, it was very time-consuming and the disk space for recording momentum matrix elements increased rapidly. The finest k point used in the irreducible Brillouin zone was 267,228. We agree that these k points may still not be enough, and extrapolation from these calculated AHC and SHC may not be suitable. Our previous studies of the anomalous Hall conductivities in *fcc* Ni [20], *hcp* Co [21] and Co-based Heusler alloys [12,22] were in good agreement with other theoretical calculations and experiments, indicating that our approaches may be reliable.

The spin polarization, P^D , of a magnetic material is usually described in terms of the spin-decomposed densities of states (DOSs) at the Fermi level (E_F) as $P^D = (N_{\uparrow}(E_F) - N_{\downarrow}(E_F)) / (N_{\uparrow}(E_F) + N_{\downarrow}(E_F))$, where $N_{\uparrow}(E_F)$ and $N_{\downarrow}(E_F)$ are the spin-up and spin-down DOSs at E_F , respectively. This cannot usually be compared with the experimental transport current results, as previously pointed out by many researchers. One simple reason for this is that for the magnetic materials, *d*-electrons give rise to the largest contributions to E_F . Nonetheless, *s*-electrons give rise to the greatest contributions to the transport current measured in the experiment. Indeed, in ferromagnets, the spin polarization of the AHE-induced Hall current, denoted as P^H , is interesting, and there are, so far, few studies on this. It is also worth mentioning that P^D may correlate with the magnetic moment of a ferromagnetic material, but is obviously independent of the magnetization direction. In this present study, we calculated the Hall current spin polarization by using $P^H = (\sigma_{xy}^{H\uparrow} - \sigma_{xy}^{H\downarrow}) / (\sigma_{xy}^{H\uparrow} + \sigma_{xy}^{H\downarrow})$, where $\sigma_{xy}^{H\uparrow}$ and $\sigma_{xy}^{H\downarrow}$ are the spin-up and spin-down Hall conductivities, respectively. Note that by definition, the absolute value of P^H can be greater than 1, while P^D is between 0 and 1. Obviously, a high Hall current spin polarization P^H of a ferromagnet is also useful. Perhaps in some magnetic materials, the spin polarization P^D of the longitudinal current is small, but the spin polarization of the laterally induced Hall current is large. Such magnetic materials could, thus, be used in spintronic devices.

3. Results and Discussion

3.1. Crystal Structure and Magnetic Properties

Table 1 shows the calculated lattice constants and total and atomic spin magnetic moments. We can see that the calculated lattice constant increased as the Cr concentration increased for both regular and inverse Heusler structures. The lattice constant was in the range between 5.672 and 5.908 Å. We can note that the lattice constants were 5.672, 5.701, 5.885 and 5.980 Å for Co₃Al, Co₂CrAl, Cr₂CoAl and Cr₃Al, respectively, in the regular structure. Obviously, this increase in lattice constant can be related to the larger Wigner–Seitz of the Cr atom. Nonetheless, the lattice constants in the XA structure became 5.723 and 5.721 Å for Co₂CrAl and Cr₂CoAl, respectively. In Co₂CrAl, the total spin magnetic moments in the XA structure were smaller than in the regular structure. However, the atomic spin magnetic moment was larger in the XA structure, resulting in a small increase in lattice constants. In Cr₂CoAl, the lattice constant in the XA structure was smaller because it is nonmagnetic, spin-unpolarized and in equilibrium.

In all our considered Co_{3-x}Cr_xAl compounds, Co₂CrAl was the only half-metal theoretically predicted by integer spin magnetization and the density of states at the Fermi level. The theoretical spin magnetic moment for Co₂CrAl is 3.00 μ_B ; however, the experimental result was only half of this [23]. In the regular Heusler alloys, the atomic positions for the two X atoms are identical, and, thus, the spin magnetic moments for the two X atoms are identical. Previous theoretical studies on Co₃Al and Co₂CrAl [24,25] reported that they are metals with spin magnetic moments of 3.90 and 3.00 μ_B , respectively, which is in good agreement with our present study. We found that the total spin moments were decreased significantly in the XA structure. The total spin magnetic moments for Co₂CrAl and Cr₂CoAl in the XA structure were 0.82 and 0.00 μ_B , respectively. The reason for the decreases in the total spin moments for Co₂CrAl, is that in the XA structure, the Cr atom is antiferromagnetically coupled with both Co atoms. The atomic spin magnetic moment for the Al atom is negative and one order of magnitude lower than the X and Y atoms. Our calculated lattice constants and magnetic moments for Cr₃Al were in very good

agreement with a previous theoretical study [26]. Nonetheless, Cr_2CoAl was reported to be ferrimagnetic, with a very small spin magnetic moment of $0.009 \mu_B$ [27].

Table 1. Calculated lattice constant a (Å), total spin magnetic moments (m^{tot}) ($\mu_B/\text{f.u.}$) and atomic (m_s) (μ_B/atom) spin magnetic moments of all considered $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds.

X_2YZ	Structure	a	m^{tot}	m_s^{X1}	m_s^{X2}	m_s^{Y}	m_s^{Al}
Co_3Al	regular	5.672	4.00, 3.90 ¹	1.25	1.25	1.71	−0.087
Co_2CrAl	regular	5.701, 5.727 ²	3.00, 1.55 ²	0.77	0.77	1.58	−0.093
	XA	5.723	0.82	0.93	1.33	−1.32	−0.035
Cr_2CoAl	regular	5.885	5.75	2.18	2.18	1.17	0.020
	XA	5.721, 5.79 ³	0.00	−	−	−	−
Cr_3Al	regular	5.908, 5.83 ⁴	2.92, 2.88 ⁴	−1.60	2.16	2.16	0.033

¹ Theoretical results, see [25]. ² Experimental results, see [6]. ³ Theoretical results, see [28]. ⁴ Experimental results, see [26].

To obtain a better understanding of the effect of Cr doping, as well as the atomic position of Cr doping on the spin magnetic moment, we can consider Co_2CrAl as an example. In regular X_2YZ Heusler alloys, the Y atom is surrounded by eight X atoms. That is to say, the Cr atom sits at the B site surrounded by eight Co atoms; see Figure 1a. In the a , b and c directions, a Z atom sits between the Cr atoms. Therefore, the covalent interactions, i.e., antiferromagnetic coupling, of the Cr d electrons are not direct. Instead, the p electrons of the Z atom interact with the Cr d electrons, which results in ferromagnetic coupling between the Co and Cr atoms. It is clear to see, in Table 1, that the spin magnetic moments for Co, Cr and Al are 0.77, 1.58 and $-0.093 \mu_B$, respectively. In the XA Co_2CrAl compound, the Cr atom sits at the C site, and the Cr atom is not surrounded by eight Co atoms. Instead, the Cr atom is surrounded by four Co and four Cr atoms; see Figure 1b. The crystal structure of bulk Cr is body-centered-cubic (bcc) and the experimental lattice constant is 2.88 Å. In bulk Cr, the Cr is surrounded by four Cr atoms, and bulk Cr is known as an antiferromagnetic material. The interatomic distance between Cr atoms is smaller compared with that in bulk bcc Cr, suggesting stronger antiferromagnetic coupling between Cr and Co atoms. Hence, the spin magnetic moments for Co, Cr and Al in XA Co_2CrAl Heusler become 0.93 (1.33), -1.32 and $-0.035 \mu_B$, respectively.

Let us examine the scalar relativistic band structures and density of states for Co_2CrAl in the regular and inverse structures, as shown in Figure 2. It is clear that Co_2CrAl in the regular structure is half-metal because there is a spin-down bandgap at the Fermi level. However, Co_2CrAl in the XA structure is a normal metal. Indeed, the spin-up or spin-down gap disappears in the energy range between -6 and 2 eV in the XA structure of Co_2CrAl . In the regular Co_2CrAl , the Cr atom is spin-spitted and at the Fermi level, and the Cr atom makes a larger contribution to the density of states than the Co atom in the regular structure. However, in the XA structure of Co_2CrAl , the Co atom (at the C site) makes the largest contribution to the spin-down density of states at the Fermi level.

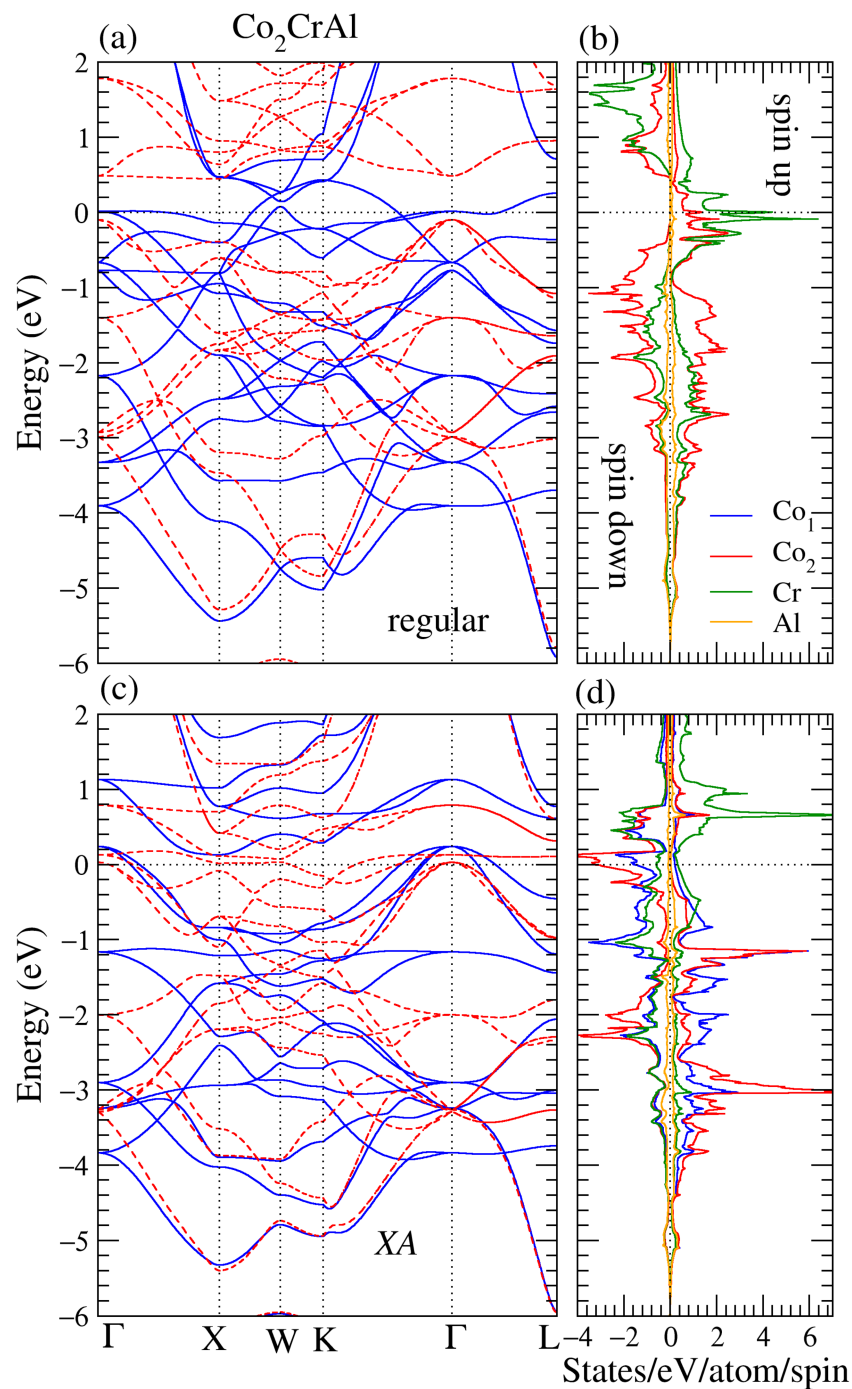


Figure 2. Left panel (a,c), scalar relativistic band structures; right panel(b,d), atom and spin decomposed density of states for Co_2CrAl in the regular and XA structures. The solid blue lines in (a,c) are for the spin-up bands, and the red-dashed lines are for the spin-down bands. The solid blue, red, green, and orange lines in (b,d) are for the two Co, Cr, and Al atoms, respectively.

3.2. Mechanical Properties

Recall that the ideal X_2YZ full-Heusler alloy is a cubic $L2_1$ structure with point group 225. Our calculated mechanical properties, together with the related physical properties of the $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds in both regular and inverse structures, are listed in Table 2. Due to the symmetric nature of the crystal structure, only three independent elastic constants— C_{11} , C_{12} and C_{44} —must be taken into account. For the $L2_1$ crystal structure, the elastic constants matrix, C_{ij} , can be represented as:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}$$

Table 2. Our calculated elastic constants C_{11} (GPa), C_{12} (GPa) and C_{44} (GPa), bulk modulus β (GPa), shear modulus G (GPa), Young's modulus E (GPa), anisotropy factor A (arb. unit) and Poisson's ratio ν (arb. unit) of all considered $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds.

X_2YZ	Structure	C_{11}	C_{12}	C_{44}	B	G_V	G_R	G	E	A	ν	B/G
					(GPa)				arb. Unit			
Co_3Al	regular	214	160	132	178	90	52	71	188	4.89	0.32	2.51
Co_2CrAl	regular	268	166	145	200	107	83	95	247	2.86	0.30	2.11
	XA	191	150	135	164	90	42	66	174	6.59	0.32	2.48
Cr_2CoAl	regular	133	141	135	138	80	−11	34	95	−	0.39	4.06
	XA	326	153	109	211	102	101	100	258	1.26	0.30	2.11
Cr_3Al	regular	254	72.4	122	133	110	107	107	256	1.35	0.18	1.24

We used the so-called stress-strain relations method to calculate these elastic constants in our density functional theoretical studies. To achieve this, depending on the symmetry of the $L2_1$ crystal structure, the total energies for some finite lattice distortions were first calculated. The stress and strain corresponding to these lattice distortions were then obtained, as well as the elastic constants. Unlike the total energy self-consistent calculations, we used a denser k -mesh of $14 \times 14 \times 14$, and the self-consistent total energy criterion was set to be as high as 1.0×10^{-8} eV, to obtain more accurate elastic constants. In the $L2_1$ crystal structure, the bulk modulus B in both Voigt (B_V) and Reuss (B_R) formalism, in terms of elastic constants, can be expressed as:

$$B = B_V = B_R = \frac{C_{11} + 2C_{12}}{3}$$

In general, Voigt is the upper bond and Reuss is the lower bond of the bulk modulus. The bulk modulus is greater than zero; therefore, $C_{11} + 2C_{12} > 0$ is one of the mechanical stability criteria in the $L2_1$ structure. The shear moduli G_V and G_R , in terms of the elastic constants in the $L2_1$ structure, are:

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}$$

Young's modulus, E , and Poisson's ratio, ν , were calculated by the following equations in terms of the bulk and shear moduli:

$$E = \frac{9BG}{3B + G} \quad \nu = \frac{1}{2} - \frac{E}{6B} = \frac{3B - 2G}{6B + 2G}$$

Poisson's ratio is a measurement of the materials that expand perpendicularly in the direction of the external compression. Our calculated nonzero elastic constants, bulk and shear moduli, Young's modulus and Poisson's ratio are all listed in Table 2.

Since our calculated elastic constants C_{ij} were all positive, the mechanical stability criteria for the cubic structure could be reduced to $C_{11} > B > C_{12}$. The calculated C_{11} , C_{12} and C_{44} for the $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds were positive, and ranged from 72.4 to 326 GPa. We found that C_{11} was 214 GPa for Co_3Al . If one Cr atom was doped to Co_3Al , the resulting C_{11} either increased or decreased, depending strongly on the crystal site of the Cr of Co_2CrAl . This crystal site dependency also occurred for Cr_3Al . The C_{11} for

Cr₃Al was 254 GPa and became 326 or 133 GPa depending on the crystal site of Co for Cr₂CoAl. This trend is very interesting. Let us take bulk modulus as an example. The bulk modulus for Co₃Al was 178 GPa. In the XA structure, when Cr was doped to the C site, the calculated bulk modulus was decreased. It was significantly increased if it became Cr₂CoAl. This trend can be roughly explained by the anisotropy factor. If the anisotropy factor is smaller, meaning that the materials have more elastic isotropy, the bulk modulus becomes larger. Nonetheless, C_{12} was also positive, ranging between 72.4 and 166 GPa. Unlike C_{11} , we found that C_{12} and C_{44} were not sensitive to Cr doping, except for C_{12} in Cr₃Al. In Co_{3-x}Cr_xAl Heusler compounds, the criterion $C_{11} > C_{12}$ was always met, except for Cr₂CoAl in the regular structure. This implies that regular Cr₂CoAl is mechanically unstable. The Zener anisotropy factor $A = 2C_{44}/(C_{11} - C_{12})$ is a dimensionless number used in the cubic system to quantify whether the material is isotropic or anisotropic. If the Zener anisotropy is 1, the material has isotropy. Our calculated anisotropy was greater than 1, meaning that the Co_{3-x}Cr_xAl Heusler compounds were all elastically anisotropic, except for regular Cr₂CoAl. Beyond this, Ranganathan et. al. [29] proposed a universal anisotropy index A^U instead of Zener anisotropy. The Zener anisotropy index is not a universal index, but is valid for the cubic phase. Since $B_V = B_R$, we also calculated $A^U (= 5 \frac{G_V}{G_R} - 5)$; the results were 3.65, 1.45, 5.71, 0.05 and 0.14 for regular Co₃Al, regular Co₂CrAl, XA Cr₂CoAl and XA Cr₃Al, respectively. It is clear that the trend for both anisotropy factors A and A^U was the same. In the cubic structure, if the anisotropy factor is negative, which indicates either $C_{11} < C_{12}$ or $C_{44} < 0$, the structure is unstable. The bulk modulus is a measurement of the volume change with respect to the external pressure. Our calculated bulk modulus was positive and ranged from 133 to 211 GPa. The ratio of the largest bulk modulus to the smallest one was 1:6, where the corresponding ratio for the shear modulus was 3:15. The bulk modulus was larger, which implies a strong resistance to volume change under pressure. Since all stability criteria were satisfied, except for regular Cr₂CoAl, we can conclude that Co_{3-x}Cr_xAl Heusler compounds are mechanically stable.

Young's modulus E can also be used to determine the stiffness of a material. If E is higher, it implies the material is stiffer. This can be seen from the definition of E as the ratio between stress and strain in the linear elastic region. The calculated Young's modulus was larger than 170 GPa, except for Co₂CrAl in the regular structure. The calculated Young's modulus of Co₃Al was 188 GPa and became 247 or 174 GPa when one Cr atom was added to the B or C site, respectively. Although the difference in E was not large, it also implies that E correlates with the atomic position. The regular Cr₂CoAl had the lowest Young's modulus of 95 GPa. Similarly, the bulk modulus for Cr₃Al was 133 GPa. If one Cr atom was replaced with a Co atom at the B or C site, the bulk modulus became 133 or 211 GPa, respectively. The G_R of regular Cr₂CoAl was negative. It resulted in a significant decrease in shear modulus G , and hence, the lowest Young's modulus E occurred.

Poisson's ratio ν is a quantity to understand the bonding characteristics of a solid. It describes the volume change in the direction perpendicular to the external force's direction. Typically, Poisson's ratio is numerically between -1 and 0.5 . The present Poisson's ratio ranged between 0.30 to 0.39 , which suggests these materials are intermetallic compounds, except for Cr₃Al, where the Poisson's ratio was 0.18 . Young's modulus, the shear modulus and Poisson's ratio satisfy the relation $G = 0.5E/(1 + \nu)$. The ratio of the bulk to the shear modulus, B/G , known as Pugh's ratio, describes the brittle or ductile behavior of materials. A high B/G ratio, >1.75 , is associated with ductility, whereas a low value ratio corresponds to brittleness. We concluded that Co_{3-x}Cr_xAl Heusler alloys could be classified as ductile materials since their B/G ratios were larger than 1.75 , except for Cr₃Al. The brittleness and ductility of a solid can also be verified by using Poisson's ratio, where $\nu < 1/3$ and $\nu > 1/3$, represent brittleness and ductility, respectively.

To describe the thermodynamic properties of a material, the Debye temperature Θ_D is a fundamental and useful parameter, correlating the elastic and thermodynamic properties of a solid. In the Debye model, it assumes that all sound waves travel at the same velocity

regardless of their wavelength. The Debye temperature can be estimated from the average elastic-wave velocity by the following equation:

$$\Theta_D = \frac{h}{k_B} \sqrt[3]{\frac{3nN_A\rho}{M}} v_m$$

where h is Planck's constant, k_B is Boltzmann's constant, N_A is the Avogadro constant, n is the number of atoms per molecule, M is the molecular weight and ρ is the density, respectively. To obtain the average sound velocity v_m , we first calculated the longitudinal and transverse sound velocities using Navier's equation; see [30] for details. The calculated density, longitudinal, transverse and average sound velocity and Debye temperature are listed in Table 3. It is clear that the longitudinal sound velocity was almost double the transverse sound velocity. Cr₃Al had the largest Debye temperature of 600 K.

Table 3. The calculated density ρ (g/cm³), longitudinal sound speed v_l (m/s), transverse sound speed v_t (m/s), average sound speed v_m (m/s) and Debye temperature Θ_D (K), d from the calculated elastic moduli.

X ₂ YZ	Structure	ρ	v_l	v_t	v_m	Θ_D
		g/cm ³		(m/s)		K
Co ₃ Al	regular	4.397	6069	3099	3472	459
Co ₂ CrAl	regular	4.182	6816	3678	4106	540
	XA	4.135	6013	3075	3445	451
Cr ₂ CoAl	regular	3.668	8115	3502	3956	504
	XA	3.993	7164	3882	4332	568
Cr ₃ Al	regular	3.492	6866	4293	4729	600

3.3. Spin and Anomalous Hall Conductivities

The calculated anomalous (σ_{xy}^A) and spin (σ_{xy}^S) Hall conductivity, as well as the Hall current conductivity ($\sigma_{xy}^{H\uparrow}$, $\sigma_{xy}^{H\downarrow}$) and spin polarization (P^D , P^H), are listed in Table 4. To obtain the theoretical AHC and SHC, we first calculated the AHC and SHC as a function of the number of k points (N_k), and the results are displayed in Figure 3. The theoretical AHC and SHC were obtained from $1/N_k \rightarrow 0$ ($N_k \rightarrow \infty$). We can note that Cr₂CoAl had the largest σ_{xy}^A ; this is because Cr₂CoAl had the largest spin magnetic moment and the intrinsic anomalous Hall effect was proportional to the spin magnetic moment of a solid. We can also note that the calculation results of AHC and SHC at specific k points fluctuated in Cr₂CoAl for the XA structure. The fluctuation may be owing to the insufficient usage of k points. There are two main sources of k points; one for obtaining the self-consistent charge density, and the other for obtaining the AHC and SHC. Table 4 also shows that σ_{xy}^S was smaller than σ_{xy}^H , except for Co₂CrAl in the inverse structure. In a half metal, the charge current will flow in only one spin channel, with no charge current in the other spin channel, thus, resulting in σ_{xy}^A being twice as large as σ_{xy}^S .

To determine how the anomalous Hall conductivities vary with the number of valence electrons, as illustrated in Figure 4, we explored the band structures, anomalous Hall conductivities and the number of valence electrons of XA Co₂CrAl and regular Cr₃Al. Figure 4b,e represent the anomalous Hall conductivity as a function of energy for the Fermi energy. We used so-called frozen band approximation to calculate σ_{xy}^A for different Fermi energies, finding that the band structures remained unchanged as the valence electrons increased or decreased. Figure 4b shows that if N_v is increased, which can be achieved by electron doping of Co₂CrAl, σ_{xy}^A decreased rapidly to around -500 S/cm. There was a large energy range, from 0 to -1 eV, where σ_{xy}^A was large, from around 400 to 1400 S/cm. This implies that electron-hole doping of Co₂CrAl was beneficial to the larger anomalous Hall conductivities. Compared with our previous studies on regular Co₂CrAl [12], we concluded that this significant change in σ_{xy}^A was due to the band pocket at the Γ point.

The band pocket (see Figure 2a in [12]) at Γ point was below the Fermi energy in regular Co_2CrAl , while the Fermi level lies between the spin-up and spin-down band pockets in XA Co_2CrAl —see Figure 4a—resulting in a large σ_{xy}^A away from the Fermi energy.

Table 4. Calculated anomalous Hall conductivity σ_{xy}^A (S/cm), spin Hall conductivity σ_{xy}^S ($\hbar\text{S}/\text{e cm}$), spin polarization P^D (%), Hall P^H (%) current spin polarization and ratio of spin current to charge current $|\eta| = \frac{(2e/\hbar)\sigma_{xy}^S}{\sigma_{xy}^A}$ of all considered $\text{Co}_{3-x}\text{Cr}_x\text{Al}$ Heusler compounds.

X_2YZ	Structure	σ_{xy}^A	σ_{xy}^S	$\sigma_{xy}^{H\uparrow}$	$\sigma_{xy}^{H\downarrow}$	P^D	P^H	$ \eta $
		(S/cm)	($\hbar\text{S}/\text{e cm}$)			%	%	
Co_3Al	regular	434	182	35	399	69	−84	0.84
Co_2CrAl	regular	155	63.3	14.2	140.8	100	63	0.82
	XA	104	370	−318	440	81	−621	7.12
Cr_2CoAl	regular	490	34.2	211	279	75	−14	0.14
	XA	−	−	−	−	0	−	−
Cr_3Al	regular	30.4	−24.0	39.2	−8.8	57	158	1.58

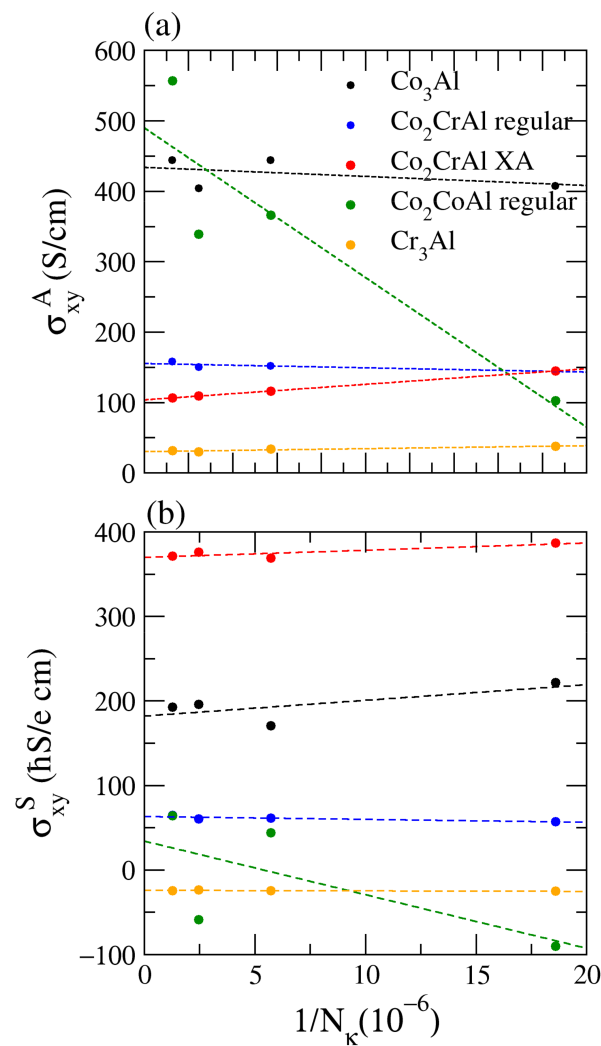


Figure 3. (a) Anomalous Hall conductivity and (b) spin Hall conductivity for $\text{Co}_{3-x}\text{Cr}_x\text{Al}$. The solid circles originate from the DFT calculations described in the manuscript and the dashed lines are the extrapolation results. The theoretical AHC and SHC are obtained from the y intercept of the dashed lines ($N_k \rightarrow \infty$).

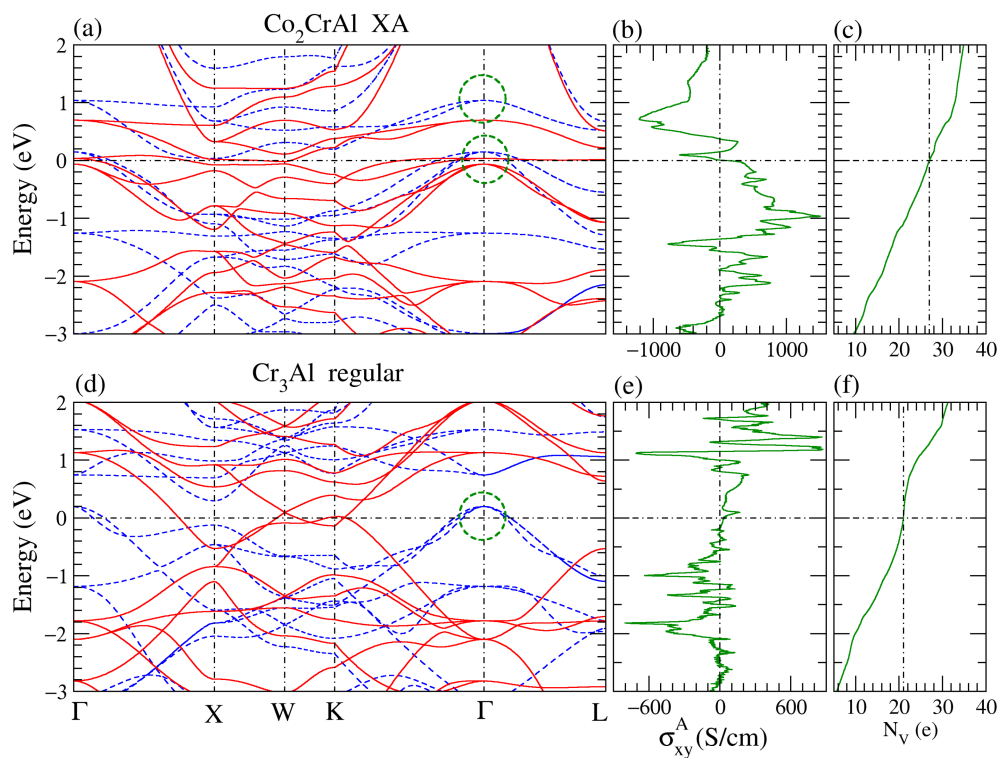


Figure 4. (a–c) Band structures, anomalous Hall conductivity and number of valence electrons of Co₂CrAl in the XA structure. (d–f) Band structures, anomalous Hall conductivity and number of valence electrons of regular Cr₃Al. Dashed blue lines are the spin-up bands, and solid red lines are the spin-down bands. The Fermi energy is shifted to zero as in the references. The green dashed circles indicate predominantly spin-up or spin-down bands, which make large contributions to the anomalous Hall conductivity.

The Hall spin polarization P^H and spin polarization P^D calculated from the electronic density of states at the Fermi level for the Co_{3-x}Cr_xAl Heusler compounds are also listed in Table 4, along with the spin-decomposed Hall conductivities ($\sigma_{xy}^{H\uparrow}$ and $\sigma_{xy}^{H\downarrow}$). The Hall spin polarization P^H is infinity in nonmagnetic materials. This is because the charge Hall current is zero in nonmagnetic materials, meaning $\sigma_{xy}^{H\uparrow} = -\sigma_{xy}^{H\downarrow}$ and, thus, $P^H = \infty$. In the Co_{3-x}Cr_xAl Heusler alloys, the spin-down Hall conductivity is larger than the spin-up Hall conductivity, except for Cr₃Al. For example, $\sigma_{xy}^{H\downarrow}$ of Co₃Al was ten times larger than that of $\sigma_{xy}^{H\uparrow}$, meaning that the Hall current carriers are mostly spin-down particles. The sign of P^H and P^D was different from those of Co₃Al, Co₂CrAl in the XA structure and Cr₂CoAl in the regular structure.

4. Conclusions

We performed a theoretical functional density study of the electronic, magnetic and mechanical properties of Co_{3-x}Cr_xAl ($x = 0, 1, 2, 3$) Heusler compounds, with generalized gradient approximation (GGA) used for the exchange correlation potential. Two principal spin-related phenomena, the anomalous Hall effect and current spin polarization of the Co_{3-x}Cr_xAl Heusler compounds in the cubic $L2_1$ structure, were discussed. Heusler compounds in two different atomic orders were considered. We found that the calculated magnetic moment of Co_{3-x}Cr_xAl decreased with an increasing Cr concentration for both ideal and inverse structures, except for Cr₃Al. We also found that the spin polarization for all Co_{3-x}Cr_xAl was larger than 50%. Both the current spin polarization and Hall current spin polarization of Co₂CrAl were high with the XA structure.

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