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Spin-Polarized Ground State Properties of Cr_2AlX (X=C, N and B) Ceramics

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ABSTRACT

The ground state structural, electronic and mechanical properties of Cr_2AlX (X=C, N and B) ceramics have been investigated by first-principles density functional pseudopotential plane-wave calculations with and without spin-polarization effects. Especially, the effects of substitutional boron atoms on the structure and properties of Cr_2AlC have been discussed in detail for the first time. All of the compounds, including newly presented Cr_2AlB are energetically and mechanically stable. From spin-polarized first-principles calculations, it is interestingly concluded that the ground states of Cr_2AlX (X=C, N and B) compounds should have magnetic character, and this assertion is supported that the theoretical results obtained from spin-polarized calculations are in excellent agreement with the experiment. Furthermore, the bonding, partial and total magnetic characteristics are explored in detail, by means of partial and total spin density of states, Mulliken atomic charges and bond overlap populations, and 2D electron density maps. Additionally, the elastic and mechanical properties are studied. And, theoretical hardnesses of Cr_2AlX (X=C, N and B) compounds are calculated, and it observed that the metallicity of the compounds plays an important role on the hardness.

Keywords: *First-principles, spin-polarization, magnetic properties, mechanical properties, hardness.*

1. INTRODUCTION

M_2AX (where M is a transition metal, A is a group A element, X is C or N) or 211 phases have attracted a considerable attention, because these material family forms a bridge between physical properties of metals and ceramics, and they have the extraordinary mechanical and physical properties such as low density, good thermal and electrical conductivity, high melting point and high thermal shock resistance [1, 2]. Cr_2AlC is a famous member of this material family. Cr_2AlC and Cr_2AlC-type compounds have been widely investigated, experimentally and theoretically [3-6]. For example, Ying et al. synthesized high purity Cr_2AlC and studied its mechanical properties [7]. Xiao et al. investigated thermal stability of Cr_2AlC [8]. Li et al. presented mechanical properties of low temperature synthesized dense and fine-grained Cr_2AlC [9]. Tian et al. fabricated single-phase Cr_2AlC samples by hot pressing of a mixture of chromium, aluminum and graphite powders, they studied its mechanical properties such as hardness, Young's modulus, flexural and compressive strength [10], and investigated its thermal and electrical properties [11]. On the other hand, Hettinger et al. explored electrical and thermal transport, and elastic properties of some M_2AlC compounds with Cr_2AlC, theoretically [12]. And also, Sun et al. calculated elastic properties of some M_2AlC compounds [13], and discussed bonding nature of the nanolayered ternary carbides with Cr_2AlC-type [14]. In another study, Sun et al. investigated energetic, structural and electronic properties of some M_2AlN compounds [15]. Finally, Cui et al. searched the

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[♠]Corresponding author, e-mail: sezginaydin@gazi.edu.tr structural and elastic properties of Cr_2AlX (X=C, N) compounds [16].

In this study, the ground state characteristics such as structural, electronic and magnetic, elastic and mechanical properties of Cr_2AlX (X=C, N and B) ceramics have been investigated by the first-principles spin-polarized density functional pseudopotential plane-wave calculations. The effects of light elements (C, N and B), especially boron for the first time, on the current properties of Cr_2AlC are studied.

2. METHOD OF CALCULATION

All calculations were performed by using first-principles density functional plane-wave pseudopotential method as implemented in CASTEP code [17]. For exchange-correlation effects, the different functionals such as GGA-PBE [18], PW91 [19], WC [20] and PBESOL [21] were used. After comparisons and tests, (*i*) the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation was selected, (*ii*) the kinetic energy cut-off was chosen as 600eV, and (*iii*) the Brillouin zone sampling was carried out using 16×16×4 *k*-points (corresponding to *k*-point separation of 0.025 1/Å), generated by Monkhorst-Pack scheme [22]. In order to modeling the interactions between ionic core and valence electrons, the ultrasoft pseudopotentials were used [23]. The structures were relaxed by using the Broyden, Fletcher, Goldfarb and Shannon (BFGS) method [24]. During the geometry optimizations, all cell parameters (atomic coordinates and lattice parameters) are relaxed, and convergence criteria were selected as 5×10^{-6} eV/atom for total energy, 0.01eV/Å for Hellmann-Feynman forces on the atoms, 0.02 GPa for max. stress and 5×10^{-4} Å for max. atomic displacement.

The cohesive energy is a measure of the strength of the forces between atom pairs in a given crystal and it gives a practical description in studying of the phase stability. The cohesive energies of Cr_2AlX (X=C, N and B) compounds are defined as the total energy of the compound minus the total energy of the isolated constituent atoms:

$$E_{coh}^{\mathrm{Cr2AlX}} = \frac{E_{final}^{\mathrm{Cr2AlX}} - \left[4E_{iso}^{Cr} + 2E_{iso}^{Al} + 2E_{iso}^{X}\right]}{8}$$

where $E_{final}^{\mathrm{Cr2AlX}}$ is the total energy of Cr_2AlX in relaxed configuration. E_{iso}^{Cr}, E_{iso}^{Al} and E_{iso}^{X} are the isolated atomic energies of Cr, Al and X atoms, respectively.

For detailed structural analysis of M_2AX phases, the distortions of the structural units can be investigated. The distortions of the octahedron (o_d) and triangular prisms (p_d) are defined as [25, 26]

$$o_d = \frac{\sqrt{3}}{2\sqrt{4z_T^2(c/a)^2+\frac{1}{12}}} \text{ and } p_d = \frac{1}{\sqrt{\frac{1}{3}+\left(\frac{1}{4}-z_T\right)^2(c/a)^2}}.$$

3. RESULT AND DISCUSSION

3.1 Ground state and structural properties

The crystal structure of Cr_2AlC is shown in Fig.1 with octahedral (Cr_6C) and prismatic (Cr_6Al) structural units, special bond and distance descriptions [16]. Its space group is $P6_3/mmc$ (No: 194) and crystal system is hexagonal. There are 8 atoms in the structure: 4 Cr atoms, 2 Al and 2 C atoms. Cr atoms are located at 4f Wyckoff positions, while Al and C atoms are located at 2d and 2a Wyckoff positions, respectively. Firstly, for more accurate ground state characterization, it is investigated that which functional is more suitable through first-principles calculations performed by using different functionals (GGA-PBE, PW91, WC, PBESOL) including spin-polarization. When experimental lattice parameters, mechanical properties and other theoretical results for Cr_2AlC are considered all together, it is observed that GGA-PBE functional is more suitable than the other functionals. Thus, GGA-PBE functional is used for all final calculations and the results are presented below.

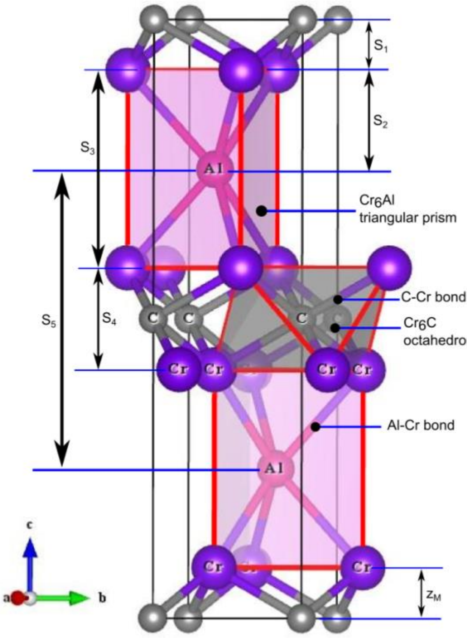

Figure 1. Crystal structure of Cr_2AlC with descriptions of structural units (octahedron and triangular prism), some special bonds and distances between the atomic layers.

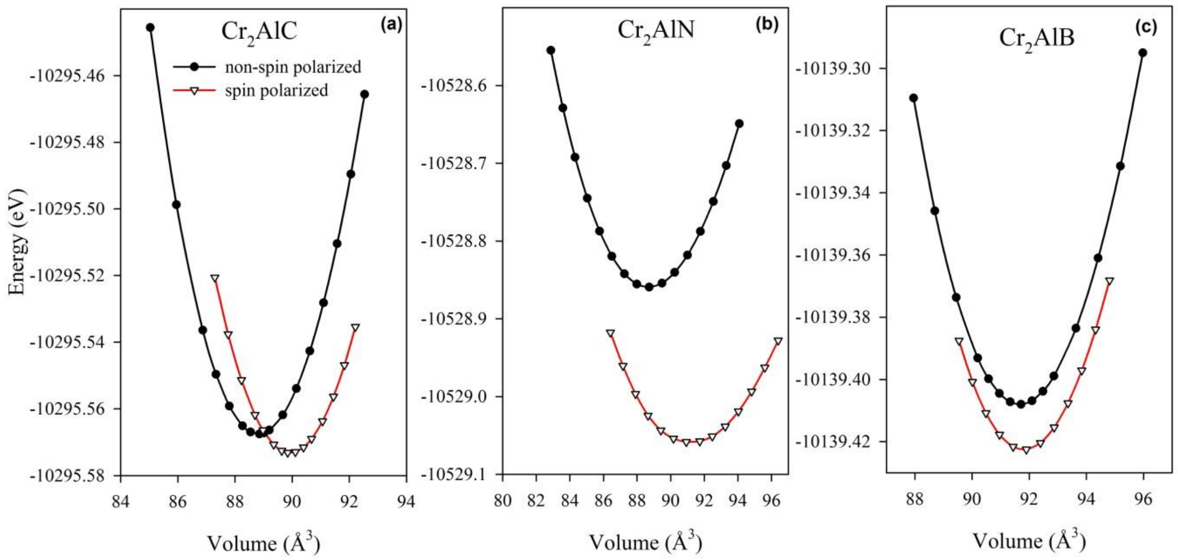

Figure 2. Calculated energy-volume curves for a) Cr_2AlC, b) Cr_2AlN and c) Cr_2AlB with and without spin-polarization effect.

Calculated energy-volume curves are presented in Fig.2(a)-(c) and calculated lattice parameters, relative final (ΔE) and cohesive energies (ΔE_{coh}) to non-spin case, integrated spin densities, special distances (S_i), inner coordinates (z_T), distortion parameters of octahedron (o_d) and triangular prism (p_d) for Cr_2AlX (X=C, N and B) ceramics are listed in Table 1 with and without spin-polarization effects. It is shown from Table 1 and Fig.2 that all compounds including new presented Cr_2AlB are energetically stable due to the negative cohesive energies, and spin-polarized cases have lower final energies and cohesive energies than non spin-polarized cases. And, the ground states of Cr_2AlX (X=C, N and B) compounds have finite integrated spin density, thus they should possess a magnetic character. Additionally, the calculated integrated spin and absolute spin densities can be used to give a practical description of the magnetic character: (*i*) if these spin density values are zero, the compound is nonmagnetic, (*ii*) if these spin density values are non-zero, finite and close each other, the compound is ferromagnetic, (*iii*) if the integrated spin density is zero and absolute spin density is nonzero, the compound is antiferromagnetic. From finite integrated spin and absolute spin density values listed in Table 1, the ground states of Cr_2AlX (X=C, N and B) compounds should be ferromagnetic.

For Cr_2AlC and Cr_2AlN, the calculated lattice parameters agree with the experimental and other theoretical results. There is no any experimental data for Cr_2AlB in the current literature, therefore any comparison couldn't be done, and the presented results for Cr_2AlB are exactly new. The calculated lattice parameters in spin-polarized cases are higher than those of non-spin cases, and they are closer to the experimental results, this situation supports cohesive energy discussion above, and then magnetic character of the ground state. Cr_2AlB has the highest *a*-lattice parameter, while Cr_2AlN has the highest *c*-lattice parameter. For detailed structural analysis, some special distances (distances between atomic layers) and distortions of the structural units are also listed in Table 1 (see Fig.1 for descriptions of the special distances, z_T is fractional coordinate). For Cr_2AlC and Cr_2AlB, it is observed that the distances in spin-polarized cases are higher than those of non-spin cases. But, this situation is little different for Cr_2AlN: S_1, S_4 and S_5 distances are higher in spin-polarized case, while S_2 and S_3 are higher in non-spin polarized case. Furthermore, the octahedrons in all compounds have less distortion in spin-polarized cases, and Cr_2AlB has the smallest o_d, Cr_2AlN follows it, and Cr_2AlC has the highest o_d. Similarly, triangular prisms in Cr_2AlC and Cr_2AlB have less distortion in spin-polarized cases, but Cr_2AlN has smaller p_d in non-spin polarized case. And, Cr_2AlB has the highest p_d. As a result of distortion analysis, it can be said that substitutional boron atoms are more influence triangular prisms than the octahedrons.

Table 1. Calculated lattice parameters with experimental ones and other theoretical results, relative final (ΔE) and cohesive energies (ΔE_{coh}) to non-spin case, spin densities, special distances (S_i) defined by Fig.1 , inner coordinates (z_T), distortion parameters of octahedron (o_d) and triangular prism (p_d) for Cr_2AlX (X=C, N and B) compounds with and without spin polarization effect.

	Cr_2AlC		Cr_2AlN		Cr_2AlB	
	Non-spin	Spin	Non-spin	Spin	Non-spin	Spin
a (Å)	2.841	2.847 2.865[a] 2.843[b] 2.858[c]	2.841	2.859 2.839[b] 2.847[d]	2.884	2.884
c (Å)	12.709	12.798 12.824[a] 12.697[b] 12.818[c]	12.694	12.954 12.708[b] 12.689[d]	12.733	12.760
V (Å^3)	88.855	89.846	88.717	91.725	91.712	91.898
ΔE (eV/unitcell)	0.000	-0.006	0.000	-0.198	0.000	-0.014
ΔE_{coh} (eV/atom)	0.000	-0.001	0.000	-0.025	0.000	-0.002
2*spin density		3.212		7.340		1.266
2*|spin density|		3.881		8.424		1.559
S_1 (Å)	1.070	1.077	1.043	1.122	1.131	1.132
S_2 (Å)	2.107	2.123	2.131	2.117	2.053	2.058
S_3 (Å)	4.214	4.246	4.262	4.234	4.105	4.116
S_4 (Å)	2.141	2.153	2.085	2.243	2.261	2.264
S_5 (Å)	6.355	6.399	6.347	6.477	6.366	6.380
c/a	4.473	4.495	4.469	4.530	4.415	4.425
z_T	0.084	0.084	0.082	0.087	0.089	0.089
o_d	1.076	1.071	1.098	1.037	1.037	1.035
p_d	1.063	1.060	1.056	1.065	1.091	1.089

[a]Experimental [10], [b]Theoretical [16],[c]Experimental [33],[d]Theoretical [15]

3.2 Density of states and magnetic properties

Calculated partial and total spin density of states for Cr_2AlX (X=C, N and B) compounds are presented in Fig.3(a)-(c) and upper side of (d). First of all, these compounds are metallic due to the finite density of states at the Fermi level. At the lower energies, DOS is originated from s-states of Al and X elements. As approaching to the Fermi level, p-states of Al and X elements, and d-states of Cr are more dominant. For [-8,-2] eV range, peaks on beta-channels of these states are closer to the Fermi level (or located at higher energies). From -2 eV to the Fermi level, alpha channels of Cr d-states make more contribution to DOS than beta-channels, and alpha channels have higher density of states than beta channels at the Fermi level. On the other hand, it is seen from Fig.3(a)-(c) that there are hybridizations between the elements: (*i*) between X p-states and Cr d-states, (*ii*) between Al p-states and Cr d-states. Because of occurring at lower energies and density of states with higher peaks, the former hybridization is stronger than the latter. It can be concluded from this expression that Cr-X bonds must exhibit better binding characteristics than Al-Cr bonds, and then Cr-X bonds must be stronger than Al-Cr bonds.

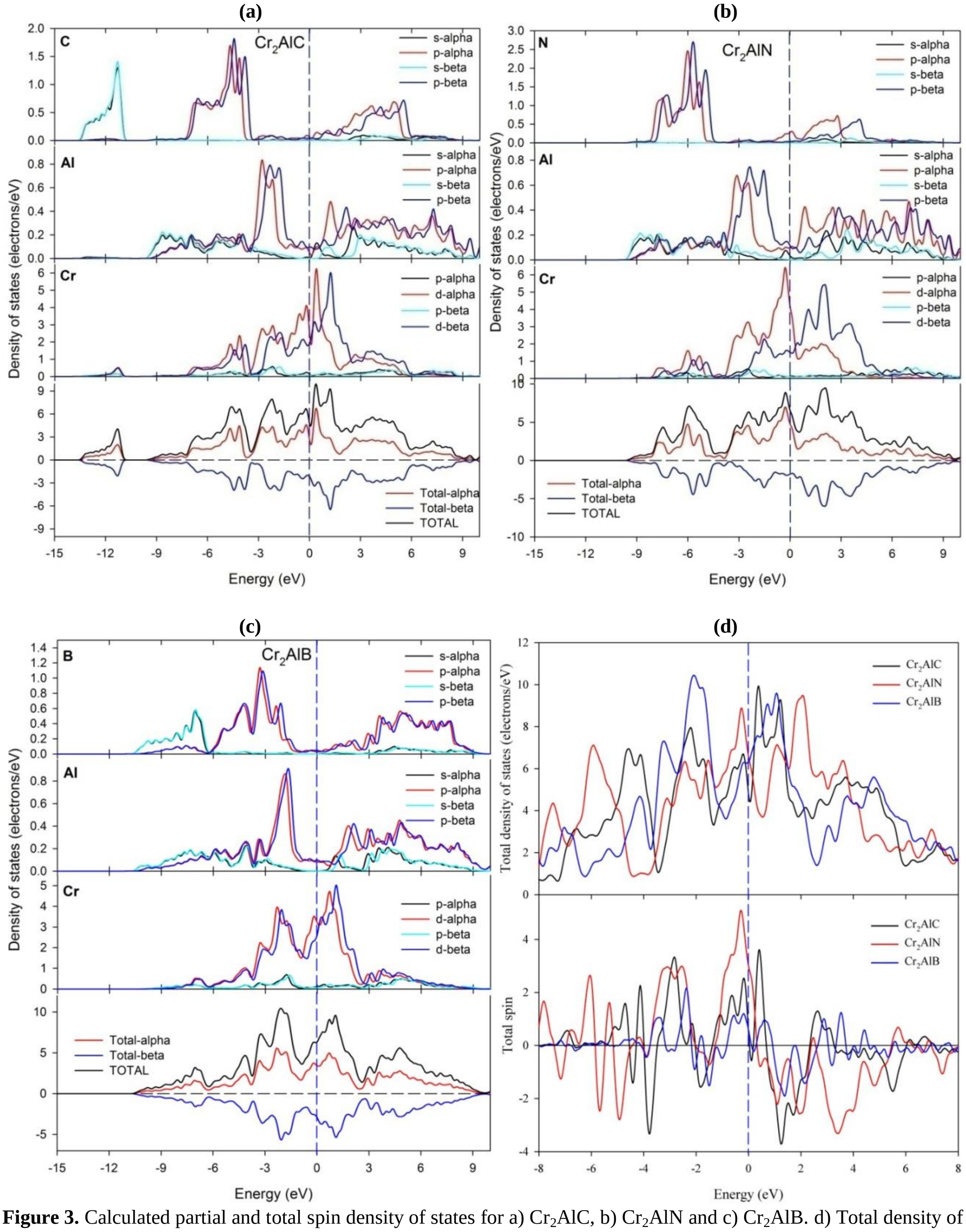
(a) (b) (c) (d)

Figure 3. Calculated partial and total spin density of states for a) Cr_2AlC, b) Cr_2AlN and c) Cr_2AlB. d) Total density of states (up) and total spin (down) for comparisons between Cr_2AlX (X=C, N and B) compounds. The Fermi level is set to zero.

Furthermore, when it is considering total alpha and beta density of states (see Fig.3(a)-(c)), it is shown that Cr_2AlX (X=C, N and B) compounds should possess magnetic character due to the anti-symmetric behavior of alpha and beta channels to horizontal energy line. For detailed magnetic character analysis, partial and total spin density of states presented in Fig.3(a)-(d) can be used to determine partial and total magnetization of the compounds. The magnetization is calculated by $M = (n_\alpha - n_\beta)\mu_B$, where n_α and n_β are number of electrons with alpha and beta spin, respectively, μ_B is Bohr magneton. n_α and n_β are determined by integrating corresponding DOS curves up to the Fermi level.

Table 2. Calculated partial and total magnetizations of Cr_2AlX (X=C, N and B) in μ_B unit.

		Cr_2AlC	Cr_2AlN	Cr_2AlB
Cr	d-alpha	11.88	13.88	10.97
	d-beta	8.24	5.74	9.46
	Total-alpha	29.71	31.86	28.69
	Total-beta	25.89	23.52	27.15
Al	p-alpha	1.68	1.57	1.73
	p-beta	1.92	2.08	1.82
	Total-alpha	2.51	2.38	2.58
	Total-beta	2.86	3.05	2.72
X	p-alpha	2.97	3.74	2.32
	p-beta	3.25	4.12	2.44
	Total-alpha	4.35	5.38	3.35
	Total-beta	4.67	5.79	3.51
	TOTAL	3.13	7.23	1.24

Calculated partial and total magnetizations of Cr_2AlX (X=C, N and B) compounds are listed in Table 2. It is observed that Cr_2AlN has the highest total magnetization, while Cr_2AlB has the smallest total magnetization (see also underside of Fig.3(d)). When it is investigated partial magnetizations, it is seen that Cr and its d-orbitals play an important role on total magnetization, and Cr atoms have higher partial magnetizations than Al and X atoms. The electron spin density maps presented in Fig.4(a)-(c) support this partial magnetic behavior. Also, X atoms have higher partial magnetizations than Al. For Cr atoms, total-alpha magnetization is higher than total-beta magnetization, but this relation is opposite for Al and X atoms. As a result of this situation, Cr atoms must possess positive spin, while Al and X atoms must possess negative spin. In this point, in order to investigate spin states of the atoms in detail (or to verify this assertion) and to obtain an information about their atomic charges and bonding nature of the compounds, Mulliken population analysis is applied and calculated results are presented in Table 3. First of all, calculated positive spin values for Cr atoms and negative spin values for Al and X atoms support the results obtained from density of states.

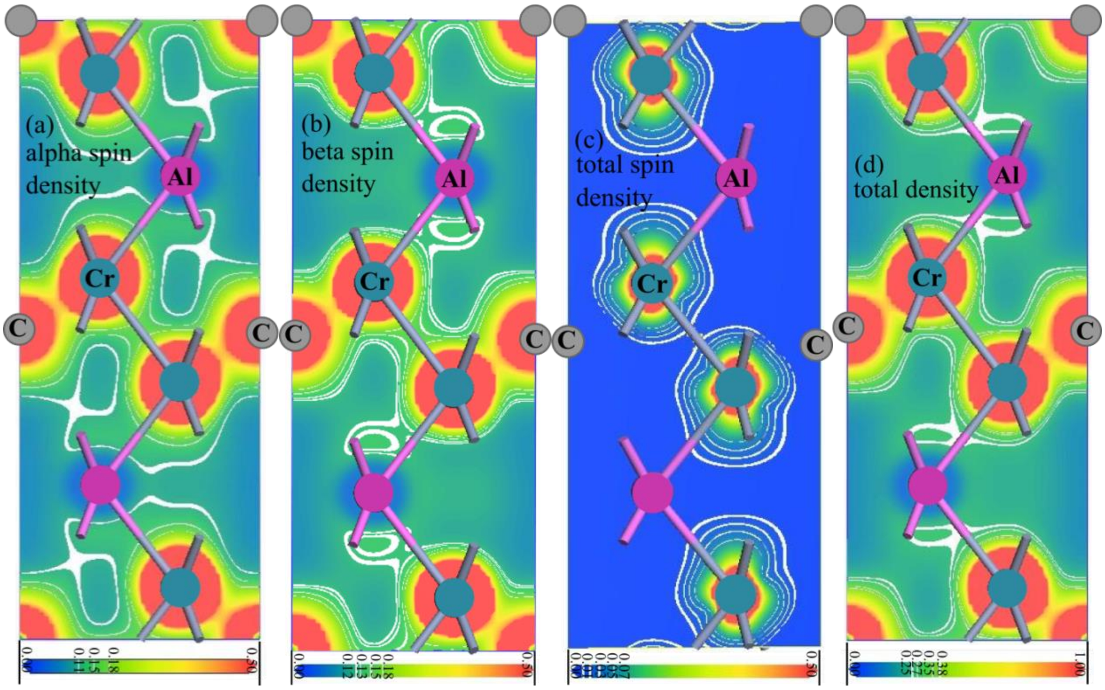

Figure 4. Spin density maps for (110) plane in Cr_2AlC: (a) alpha- (b) beta-, (c) total spin density, and (d) total electron density. Electron density is high (low) in red (blue) colored regions.

Table 3. Calculated partial and total Mulliken atomic charges and spins for the elements in Cr_2AlX (X=C, N and B) compounds with orbital contributions.

		Cr_2AlC		Cr_2AlN		Cr_2AlB	
		Non-spin	Spin	Non-spin	Spin	Non-spin	Spin
Cr	s	2.14	2.14	2.18	2.21	2.10	2.10
	p	6.67	6.68	6.66	6.68	6.70	6.70
	d	5.10	5.08	5.05	4.96	5.16	5.15
	Total	13.91	13.90	13.89	13.85	13.96	13.96
	Charge	0.09	0.10	0.11	0.15	0.04	0.04
	Spin		0.48		1.05		0.19
Al	s	0.88	0.88	0.87	0.89	0.88	0.88
	p	1.82	1.81	1.80	1.83	1.78	1.78
	Total	2.69	2.69	2.67	2.72	2.65	2.66
	Charge	0.31	0.31	0.33	0.28	0.35	0.34
	Spin		-0.09		-0.17		-0.03
X	s	1.40	1.40	1.64	1.65	1.04	1.04
	p	3.10	3.11	3.91	3.93	2.38	2.38
	Total	4.50	4.51	5.55	5.58	3.43	3.43
	Charge	-0.50	-0.51	-0.55	-0.58	-0.43	-0.43
	Spin		-0.08		-0.10		-0.04

From Table 3, each atom has the highest spin values in Cr_2AlN, while they have the smallest spin values in Cr_2AlB (as absolute value). When calculated atomic charges are considered, it is observed that Cr and Al atoms have positive charges with and without spin effects, while X atoms have negative charges. This indicates that binding in Cr_2AlX (X=C, N and B) compounds should possess an ionic component at least. Otherwise, when calculated bond overlap populations are considered (see P^{μ} column of hardness calculation in the next section), it is seen that Cr-X and Al-Cr bonds have positive bond populations, and therefore there are bonding interactions between Cr and X, and Al and Cr. This result supports DOS interpretation above. Generally, populations of Cr-X bonds are higher than Al-Cr bonds, thus the covalency of Cr-X bonds are higher than Al-Cr bonds, and the binding in Cr_2AlX (X=C, N and B) compounds also includes a covalent component. Additionally, the electron density maps in Fig. 4(a), (b), and (d) verify this bonding nature. It is known that the electron density with spherical symmetry centered at the atoms indicates ionic bonding, while electron density lying along the bond indicates covalent bonding, and other spatial representations of electron density indicate metallic bonding.

3.3. Elastic and mechanical properties

For hexagonal crystal systems, there are five independent elastic constants (c_{11}, c_{33}, c_{44}, c_{12} and c_{13}), and they must satisfy Born stability criteria given by **(*i*)** $c_{44}>0$, **(*ii*)** $c_{11}>|c_{12}|$, **(*iii*)** $(c_{11}+c_{12})c_{33}>2(c_{13})^2$ for mechanical stability [27]. We computed single-crystal elastic constants of Cr_2AlX (X=C, N and B) compounds within stress-strain technique [28], the results are listed in Table 4. It is observed that all compounds with boron-including one satisfy the conditions above, therefore they are mechanically stable. For Cr_2AlC and Cr_2AlB, non-spin polarized elastic constants and mechanical properties are higher than those of spin-polarized case. And, this situation is partially valid for Cr_2AlN, because non-spin polarized c_{13} and c_{44} are smaller than those of spin-polarized case. Furthermore, calculated elastic constants and mechanical properties agree with the available theoretical results. However, it is interesting that calculated Young's modulus in spin-polarized case of Cr_2AlC is in good agreement with the experimental value, this result supports the idea that the ground state of Cr_2AlC is spin-polarized (or has a magnetic character). In spin polarized case, Cr_2AlN has the highest bulk modulus, while Cr_2AlB has the highest shear and Young's moduli.

Table 4. Calculated elastic constants (c_{ij}), bulk (B), shear (E) and Young's (E) moduli of Cr_2AlX (X=C, N and B) compounds with and without spin polarization effect.

	Cr_2AlC		Cr_2AlN		Cr_2AlB	
	Non-spin	Spin	Non-spin	Spin	Non-spin	Spin
c_{11}	394.3 384^a 369^b 396^c	333.1	253.4 282^b	197.4	323.0	302.6
c_{33}	352.1 382^a 355^b 382^c	344.1	320.5 362^b	320.9	311.5	271.7
c_{44}	138.0 147^a 143^b 173^c	103.8	76.0 77^b	92.1	162.3	155.7
c_{12}	103.9 79^a 77^b 117^c	53.9	50.0 85^b	43.8	94.1	78.4
c_{13}	109.1 107^a 102^b 156^c	105.1	90.9 141^b	94.9	141.8	110.2
B	198.1 193^a 184^b 226^c	170.3	141.2 181^b	124.7	190.0	163.8
G	138.6 148^a 141^b 145^c	118.0	89.3 87^b	83.1	122.0	119.6
E	337.2	287.5 288^d	221.3	204.1	301.5	288.6

[a]Theoretical [2], [b]Theoretical [16],[c] Theoretical [13],[d]Experimental [10]

Additionally, hardness is one of the important mechanical properties and can be calculated by some theoretical methods. The microhardnesses of the structures are calculated by the method which was proposed by Guo et.al [29]. As a difference from the other theoretical hardness methods [30, 31], metallicity of the compounds, and more specifically, effects of d-electrons which can be important in transition metal-including structures are considered, and then more accurate results can be obtained. In this method, hardness of a binary system is given by

$$H_v^\mu = A_0 \left(N_e^\mu\right)^{2/3} (d^\mu)^{-2.5} e^{-1.191 f_i^\mu - 32.2 \left(f_m^\mu\right)^{0.55}}$$

where A_0 is a constant, and it is equal to 1051 (or 350) for bonds with (or without) d-valence electrons. d^μ and N_e^μ are bond length and valence electron density, respectively. f_i^μ and f_m^μ are bond ionicity and metallicity, respectively. And, the hardness of a complex compound can be expressed as the geometrical average of hardness of all binary systems, namely, total hardness of the compound is

$$H_v = \left[\prod_\mu \left(H_v^\mu\right)^{n^\mu}\right]^{1/\sum n^\mu}$$

where n^μ is the number of binary bond systems in the complex compound. The detailed information and other theoretical formulae about the method can be found in Ref. [32].

Table 5. Calculated Vickers hardness and related parameters of Cr_2AlX (X=C, N and B) ceramics with metallicity effect.

		d^μ	N^μ	P^μ	N_e^μ	f_i^μ	$f_m^\mu(\times10^{-3})$	H_v^μ	H_v
Cr_2AlC	C-Cr	1.965	12	0.980	0.790	0.192	8.2	13.3	5.1 5.2^a
	Al-Cr	2.685	12	0.280	0.279	0.438	9.3	1.9	
Cr_2AlN	N-Cr	1.996	12	0.840	0.824	0.369	7.2	12.6	5.3
	Al-Cr	2.685	12	0.250	0.277	0.386	8.8	2.2	
Cr_2AlB	B-Cr	2.013	12	0.960	0.641	0.219	9.1	9.3	4.1
	Al-Cr	2.647	12	0.370	0.282	0.526	9.2	1.8	

[a]Experimental [10]

Calculated theoretical hardnesses of Cr_2AlX (X=C, N and B) compounds are listed in Table 5 with bond lengths, Mulliken overlap populations and other related parameters. It is shown that calculated hardness of Cr_2AlC is in excellent agreement with the experimental value (5.2 GPa, Ref.[35]). Cr_2AlN has the highest hardness, while Cr_2AlB has the smallest hardness. And, Cr-X bonds are harder than Cr-Al bonds due to the lower bond length, bond ionicity (f_i) and metallicity (f_m), and higher bond overlap populations. As a result of possible comparisons between hardness and bulk, shear and Young's moduli, it isn't observed any direct relation between hardness and bulk modulus, shear modulus, Young's modulus. Otherwise, the hardness of the compounds are calculated by other methods in Ref.[30] and [31] which are not including metallicity, and it isn't obtained reasonable results. Therefore, it can be said that the metallicity is an important parameter for hardness of Cr_2AlX (X=C, N and B) compounds.

4. CONCLUSION

The ground state structural, electronic and mechanical properties of Cr_2AlX (X=C, N and B) ceramics have been investigated by first-principles density functional pseudopotential plane-wave calculations with and without spin-polarization effect. It is shown that all compounds including newly presented Cr_2AlB are energetically and mechanically stable, and their ground states calculations performed by using different functionals revealed that they have finite spin density, thus the ground states of well-known members of 211-phases (Cr_2AlC and Cr_2AlN) with Cr_2AlB should possess a magnetic character (ferromagnetism). Other calculated properties such as structural, electronic and mechanical properties and available experimental data support this ground state magnetic behavior. From partial density of states, Mulliken populations, hardness analysis and electron density maps, Cr-X bonds exhibit better binding characteristics than Al-Cr bonds, and then Cr-X bonds must be stronger than Al-Cr bonds. And, the binding in Cr_2AlX (X=C, N and B) compounds include ionic, covalent and metallic components.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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