

Exploring the Elastic and Electronic Properties of Chromium Molybdenum Diboride Alloys

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ABSTRACT

We perform first-principles calculations to study the structural, mechanical, thermal, electronic, and magnetic properties of $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ for $x = 0.25, 0.33, 0.50, 0.67$ and 0.75 . Based on structural search methods, we determine the ground-state structure for each concentration. The ternaries are either monoclinic ($x = 0.25, 0.75$) or trigonal ($x = 0.33, 0.50, 0.67$). The calculated mechanical properties reveal that the strength of $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ is maximized for $x = 0.50$. $\text{Cr}_{0.5}\text{Mo}_{0.5}\text{B}_2$ exhibits excellent mechanical properties ($B = 298$ GPa, $Y = 558$ GPa, $G = 235$ GPa, $\nu = 0.19$, $H_v = 27$ GPa), surpassing those of $\beta\text{-MoB}_2$ at a lower cost. All of these ternaries are hard alloys with Vickers hardness greater than 24 GPa. Chemical bonding analysis demonstrates that the strength of the new compounds is related to the alternating planar and buckled B-B layers, as well as the strong TM-B bonds. The enhanced strength of $\text{Cr}_{0.5}\text{Mo}_{0.5}\text{B}_2$ is a consequence of the high density of strong interlayer Cr-Mo metallic bonds around the Fermi level.

1. Introduction

Metal borides have been widely studied because they exhibit excellent mechanical properties [55, 73, 46, 71], high melting points [36], hardness [24, 33, 19], magnetism [7, 25, 40, 16] and even superconductivity [41]. Most transition metal borides (TMBs) are known to be hard, and a few of them (for example, WB_4 , ReB_2 , YB_{12} , and ZrB_{12}) stand out as superhard materials with Vickers hardness exceeding 40 GPa [14]. Combined with their high-melting points and chemical inertness [55], TMBs are considered outstanding materials for wear-intensive, high-temperature, and corrosion resistance applications [1]. Most importantly, metal borides can easily be industrially synthesized under ambient temperature and pressure conditions, which is a substantial technological advantage in comparison with other strong (e.g. carbon-based) materials [33]. Despite their metallic nature, TMBs owe their strength to the covalent B-B bonds, which are similar to carbon in its diamond structure [49]. Other factors also contribute to the high mechanical properties of these compounds, in particular the strength of the TM-B bonds (TM = transition metal), and the direction and arrangement of the atomic bonds in the crystal structure [47].

Magnetism in TMBs originates from the TM elements, and the contribution of the boron is to stabilize the crys-

tal phase, creating a number of common motifs found in many different boron metalloids [1]. $\text{Nd}_2\text{Fe}_{14}\text{B}$ is one of the strongest permanent magnets ($3.3 \mu_B/\text{Nd}$) in the boride family [1, 42]. Among the TM diborides, CrB_2 [7] and MnB_2 [25] exhibit magnetic ordering, similarly to other rare earth diborides such as TbB_2 and DyB_2 [40, 16].

Superconductivity has also been observed in diborides such as MgB_2 ($T_c = 39$ K), OsB_2 ($T_c = 2.1$ K) and RuB_2 ($T_c = 1.6$ K) [7, 68]. Among these, MgB_2 caught special attention due to its high transition temperature, the highest known for a type-I superconductor [1] at ambient pressure. In all these cases, the electron-phonon interaction is the driving force for the observed superconductivity. These examples demonstrate the large diversity of material types and different applications involving metals and B-B bonds.

Hardening and strengthening metals by alloying is a well-known method to improve the mechanical properties of metallic systems [10]. For the particular case of metal rich borides, explorations in ternary systems to increase the overall strength have received special attention in recent years. Compounds like Mo_2FeB_2 , Mo_2NiB_2 , WCoB , and others, have been explored, exhibiting excellent mechanical properties [20, 52, 2]. Motivated by these results, some of these compounds have been further alloyed, adding small amounts of TM impurities to maximize their strength [69, 74, 60].

Little has been reported so far for the Cr-Mo-B ternary system. Yu et al. synthesised and studied the crystal structure, microhardness, electrical resistivity, and oxidation resistivity in air of $(\text{Cr}_{0.85}\text{Mo}_{0.15})\text{B}_4$ [72, 44]. Later in 2010, Tojo et al. performed a first-principles thermodynamic analysis to clarify the phase equilibria in the Cr-Mo-B ternary system [65]. In that study, they only considered the $(\text{Cr},\text{Mo})\text{B}_2$ AlB_2 -type crystal phase. It is surprising that the $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$

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ternary diboride system has not yet been studied more in depth, considering the excellent mechanical properties of MoB₂ [73] and the successful use of Cr as a dopant to improve the mechanical properties in certain alloys [69, 60, 28].

In this paper we carry out an ab initio study of the effects of the alloying concentration on the mechanical properties of Cr_{1-x}Mo_xB₂. Instead of starting with the well-known hexagonal AlB₂-type phase, we will use structural search methods that can explore all low energy phases, avoiding the biases and constraints of other methods towards specific crystal structures. Our main objective is to maximize the mechanical strength of the ternary as a function of the alloying concentration and to determine the distribution of new phases. We considered concentrations of $x = 25\%$, 33% , 50% , 67% and 75% . The structural, mechanical, thermal, electronic and magnetic properties of these alloys are studied at different concentrations.

2. Methods

First-principles calculations were performed to study the behavior of Cr_{1-x}Mo_xB₂ alloys in the framework of density functional theory (DFT) [27]. The exchange and correlation effects were treated using the Generalized Gradient Approximation (GGA) with the parameterization of Perdew-Burke-Ernzerhof (PBE) [48]. The valence electrons wave functions were described by the projector augmented-wave (PAW [8]) method and expanded up to a cutoff energy of 800 eV. The PAW pseudo-potentials considered three valence electrons for B and fourteen for Cr and Mo, including the d-orbitals. To sample the irreducible Brillouin zone of each structure, we used a gamma-centered k-point mesh with the Monkhorst-Pack scheme [39]. The total energy in each cell was optimized for a maximum error of 0.1 meV/atom. The Kohn-Sham equations were solved self-consistently with a maximum total energy difference of 10^{-6} eV. The calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [30, 29].

For each starting stoichiometry, the Minima hopping search method was used to find the ground state structures for each stoichiometry [18, 3]. This methodology has been successfully used to construct the convex hulls of many different alloy systems, such as BiSb [56], LiSi [67], or NaAu [53].

From the resulting relaxed structures we select those with low formation energy, and calculate the elastic constants from the stress-strain relationship, when introducing finite distortions in the crystal lattices, as implemented in the VASP code. The mechanical properties such as bulk modulus (B), Young's modulus (Y), shear modulus (G) and Poisson's ratio (ν) were calculated from the elastic tensor using the ELATE software [17]. The thermal properties, which describe the temperature dependence of the volume (V), bulk modulus (B), linear coefficient of thermal expansion (α) and Debye temperature (θ_D), were calculated using the Debye Quasi-harmonic model implemented in the Gibbs2 code [51]. The phonopy package [63] was used to calculate the specific heat capacity (C_v). The chemical bonding was investigated using

the COHP analysis as implemented in the LOBSTER program [35].

To investigate the magnetism of Cr_{1-x}Mo_xB₂, total energies were calculated considering a ferromagnetic and an antiferromagnetic (AFM) phase. For the AFM calculations, the spins are chosen to alternate the orientation along the z-axis layers (up/down/up... and so on), similar to the AFM behavior of CrB₂.

3. Results and discussion

3.1. Binary Systems

Table 1

Bulk modulus (B in GPa), Young's modulus (Y in GPa), Shear modulus (G in GPa), Poisson's ratio (ν) and Vickers hardness (H_v in GPa) for various materials.

Material	B	Y	G	ν	H_v
Tungsten	323 ^a	407 ^b	160 ^b	0.28 ^b	
Steel	168 ^a	207 ^b	83 ^b	0.30 ^b	
Mo ₂ FeB ₂	309 ^c	500 ^c	204 ^c	0.23 ^c	24.6 ^c
Mo ₂ NiB ₂	330 ^c	469 ^c	186 ^c	0.26 ^c	19.3 ^c
WCoB	330 ^d	492 ^d	196 ^d	0.25 ^d	45.0 ^e
Ni-Cr-Mo	229 ^f	267 ^f	102 ^f	0.30 ^f	
CrB ₂	240 ^g	423 ^g	175 ^g	0.21 ^g	16.0 ^h
α -MoB ₂	317 ⁱ	463 ^j	186 ^j	0.28 ^k	15.2 ^j
β -MoB ₂	299 ⁱ	522 ^j	216 ^j	0.19 ^l	22.0 ^j
	334 ^m				21.7-24.7 ⁿ

^a Ref. [26] Experimental

^b Ref. [10] Experimental

^c Ref. [20] Theoretical

^d Ref. [74] Theoretical

^e Ref. [52] Experimental

^f Ref. [6] Theoretical

^g Ref. [46] Experimental

^h Ref. [70] Experimental

ⁱ Ref. [61] Experimental

^j Ref. [62] H_v Experimental, Y and G Theoretical

^k Ref. [55] Theoretical

^l Ref. [73] Theoretical

^m Ref. [34] Experimental

ⁿ Ref. [43] Experimental

The space group 191 for AlB₂ is a structure typical of many borides. In this crystal phase, the boron atoms form honeycomb layers and the aluminum atoms sit between them at the center of the hexagons in alternate layers. If electrons are assumed to be transferred completely from the aluminum layer to the boride layer, then, the boron layer is isoelectronic with graphite [9]. When the intercalated layer transfers more electrons to the honeycomb layer than those required to be isoelectronic with graphite, the planar sheet becomes buckled, as in the case of RuB₂ [11]. In either case, the stacking between the different layers is always the same, one honeycomb boron layer and an intercalated layer, which is the A metal atom in the chemical formula AB₂.

Chromium diboride exhibits a hexagonal AlB₂-type crystal structure with space group P6/mmm (191) [55]. Like

other TMBs, it has excellent mechanical properties, surpassing those of regular steel (see Table 1). It is considered a hard material ($H_v = 16$ GPa) [70] and has a high melting point (2473 K) [45]. As a result CrB_2 is considered suitable for corrosion/wear resistant applications [13, 12, 5, 23]. CrB_2 is an itinerant antiferromagnet with a Néel temperature of 88 K and an effective magnetic moment of $2.1 \mu_B$ per unit cell [7]. The calculated lattice parameters for this binary are presented in Table 2 and they are in good agreement with the experimental values. To describe the magnetic behavior of the compound, spin-polarized calculations were performed with GGA-PBE, SCAN [59], and HSE06 [31] functionals. The magnetic moment per Cr atom in each case was of $1.281 \mu_B$, $2.115 \mu_B$ and $2.389 \mu_B$, respectively. Since the most accurate results were obtained with SCAN, all the subsequent magnetic calculations for the ternary systems were performed with this functional.

Molybdenum diboride has two different structures: a hexagonal high-temperature phase $\alpha\text{-MoB}_2$ with space group $P6/mmm$ (191), and a trigonal low-temperature phase $\beta\text{-MoB}_2$ with space group $R\bar{3}m$ (166) [62]. $\beta\text{-MoB}_2$ is the most stable phase, and $\alpha\text{-MoB}_2$ is a meta-stable phase that can be easily transformed to $\beta\text{-MoB}_2$ with protracted annealing [61]. However, experimental results have demonstrated that both structures are stable at atmospheric conditions [62]. The structures of $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$ are very similar in the sense that they both have alternating layers of molybdenum and boron. $\beta\text{-MoB}_2$ displays alternating planar and buckled hexagonal boron layers. In the buckled layers, the molybdenum atoms will not sit at the center of the hexagons, but instead on top of a boron atom. The buckled boron layers are responsible for the increase in hardness and mechanical properties of $\beta\text{-MoB}_2$ with respect to $\alpha\text{-MoB}_2$ [61]. Still, both $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$ have excellent mechanical properties, even exceeding those of tungsten (see Table 1). MoB_2 is a non-magnetic material [36]. In Table 2 we present the calculated lattice parameters for both structures. Our results for $\beta\text{-MoB}_2$ are in excellent agreement with the experimental data, with an error smaller than 1%. The values for $\alpha\text{-MoB}_2$ are in good agreement with experimental data (a bit farther than the β phase) and close to other theoretical studies [55, 71].

3.2. Ternary Systems

The results of the structural search for the ternary systems are presented in Table 2 and Figure 1. We can observe that none of the ternary systems presents a pure AlB_2 type of crystal structure as the ground state. All of the low energy phases are similar to $\beta\text{-MoB}_2$, with alternating flat and buckled B layers. For the 25% and 75% concentrations, the most stable structures are monoclinic, while for the rest (33%, 50%, and 67%), they are trigonal, like $\beta\text{-MoB}_2$. More specifically, $\text{Cr}_{0.67}\text{Mo}_{0.33}\text{B}_2$ and $\text{Cr}_{0.33}\text{Mo}_{0.67}\text{B}_2$ exhibit a $P3$ -type symmetry, which is different from the $R\bar{3}$ -type symmetry observed in $\text{Cr}_{0.50}\text{Mo}_{0.50}\text{B}_2$ and $\beta\text{-MoB}_2$. In the trigonal phases, Cr and Mo atoms are always placed in independent layers along the stacking direction. The monoclinic

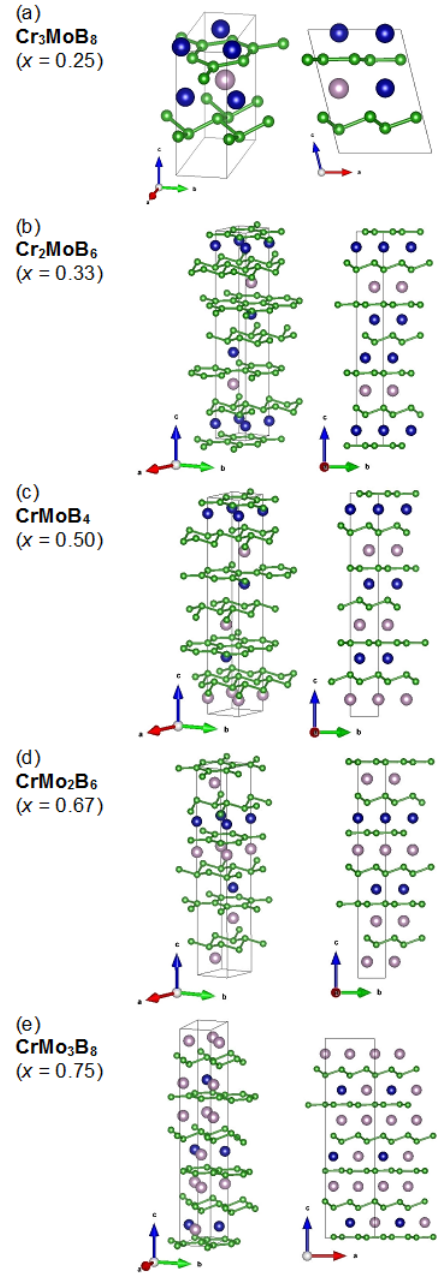


Figure 1: Crystal structures of $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ for $x = 0.25, 0.33, 0.50, 0.67$ and 0.75 . B atoms in green, Mo atoms in pink and Cr atoms in blue. Images generated using VESTA [38].

phases have layers which mix both Cr and Mo atoms, modifying the symmetry of the crystalline systems. The lattice parameters and angles for the conventional cells of the new ternary systems are also presented.

The lowest formation energies are negative for all the compound stoichiometries, confirming their chemical stability. The previous analysis was complemented by building the convex hull for the $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ system to test the chemical stability of the phases against each other at zero temperature and zero pressure. The results are presented in Figure 2. As observed, the 25% and 33% structures are on the convex hull indicating they are chemically stable phases.

Table 2

Stoichiometry, crystal system, number of atoms in the conventional cell (Atoms), space group name and number in the Hermann–Mauguin notation (spg), formation energy per atom (E_f), conventional cell axes (a, b, c) and angles (α, β, γ) for the ternary systems $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$. Letter x represents the concentration of Mo. Calculated, experimental and theoretical data for the binary systems CrB_2 ($x = 0.00$) and MoB_2 ($x = 1.00$) is presented for comparison.

Stoich.	x	System	Atoms	spg	E_f (eV)	a (Å)	b (Å)	c (Å)	α	β	γ
CrB_2	0.00	Hexagonal	3	P6/mmm (191)	-0.383	2.953	2.953	3.027	90°	90°	120°
					-0.323 ^a	2.975 ^b	2.975 ^b	3.066 ^b			
Cr_3MoB_8	0.25	Monoclinic	12	P1m1 (6)	-0.403	5.094	2.941	6.788	90°	105°	90°
Cr_2MoB_6	0.33	Trigonal	18	P $\bar{3}$ m1 (164)	-0.416	2.952	2.952	19.795	90°	90°	60°
CrMoB_4	0.5	Trigonal	18	R3m (160)	-0.421	2.971	2.971	20.085	90°	90°	120°
CrMo_2B_6	0.67	Trigonal	18	P3m1 (156)	-0.428	2.987	2.987	20.388	90°	90°	120°
CrMo_3B_8	0.75	Monoclinic	36	P1m1 (6)	-0.418	2.996	5.186	20.595	90°	90°	90°
α - MoB_2	1.00	Hexagonal	3	P6/mmm (191)	-0.288	3.035	3.035	3.315	90°	90°	120°
					-0.307 ^a	3.045 ^c	3.045 ^c	3.071 ^c			
β - MoB_2	1.00	Trigonal	18	R $\bar{3}$ m (166)	-0.442	3.019	3.019	20.975	90°	90°	120°
						3.012 ^c	3.012 ^c	20.943 ^c			
						3.014 ^d	3.014 ^d	20.961 ^d			

^a Ref. [71] Theoretical WIEN2k code

^b Ref. [70] Experimental

^c Ref. [62] Experimental

^d Ref. [43] Experimental

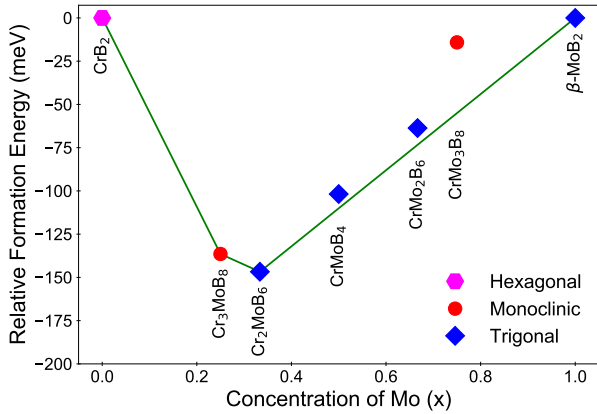


Figure 2: Convex hull (in green) for the $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ system.

The ground state phases for 50% and 67% are not lying exactly on the convex hull, however, they are very close and the difference in energy can be attributed to the numerical accuracy of DFT calculations. The 75% structure is not on the hull, indicating it is a metastable phase. Since there have been no previous experimental or theoretical reports, our results are predictions for these structures, which we hope will stimulate experimental investigation and corroboration.

A crystal system is considered dynamically stable if its potential energy increases for any change in its atomic positions. This condition is verified when all phonons have real and positive frequencies [64]. The phonons for the predicted ternary diborides are all positive, confirming the dynamical stability of these compounds. In Figure 3 we show the phonon spectra and the contributions of the different species to the phonon mode density of states for $x = 0.50$. The

phonons and atom projections for all of the binaries and ternaries are presented in the supplemental information. For all the compounds, the Cr and Mo atoms are responsible for the low-frequency vibrations, and the B atoms for the high-frequency vibrations (greater than 10 THz). In the low frequency range, we observe a main (zone boundary) acoustic peak which moves down in frequency from 8 THz to 5 THz as the percentage of Mo is increased to 100%. The acoustic modes are contributed proportionally by both transition metals. Several almost dispersionless manifolds of optical-like vibrations of Cr or B planes develop at higher frequencies. In particular an isolated Cr peak around 10 THz is visible in most of the alloys. $\text{Cr}_{0.25}\text{Mo}_{0.75}\text{B}_2$, on the other hand, has a phonon frequency gap around 10 THz: with mixed TM layers, there are no isolated Cr modes and the equivalent hybrid mode is a bit lower in frequency. For $\text{Cr}_{0.75}\text{Mo}_{0.25}\text{B}_2$ the mode is dominated by Cr and almost split off in frequency from the acoustic manifold. For frequencies greater than 11 THz, the B atoms dominate the vibrations in the crystal structures, and the Cr and Mo atoms are almost motionless. This range combines dispersionless modes characteristic of isolated B planes, with dispersing bands contributed by inter-plane interactions mediated by TM motions (visible e.g. around 15 THz). These dispersing bands can have group velocities similar to the acoustic bands and will contribute significantly to thermal conductivity at higher temperature.

3.2.1. Mechanical Properties

Table 3 lists the values of the relevant elastic constants for each structure. The complete elastic tensors may be consulted in the supplemental information. The mechanical properties such as bulk modulus (B), Young's modulus (Y), shear modulus (G), and Poisson's ratio (ν) were computed with the elastic constants and the results are shown in Table 4. The

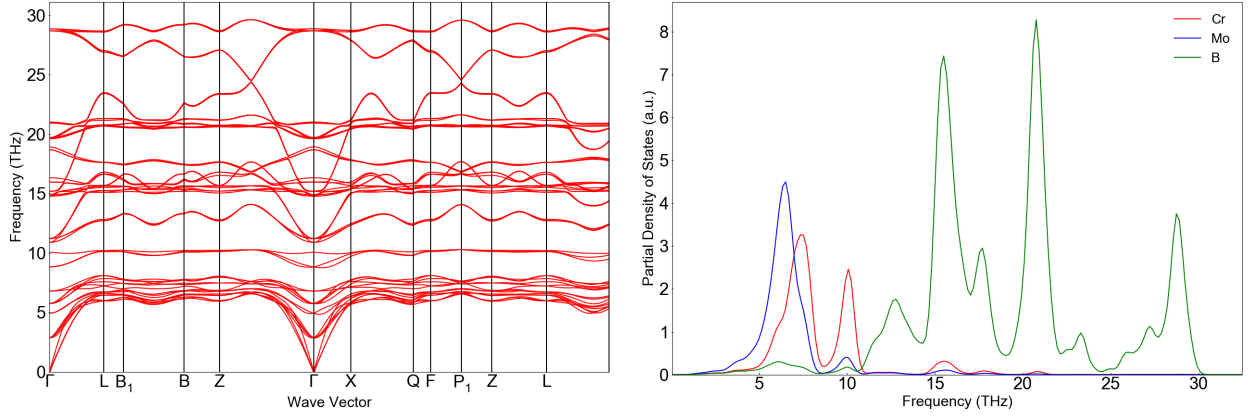


Figure 3: (left side) Phonon spectra and (right side) ionic contribution to phonon density of states of the different species in the trigonal structure (space group 160, R3m) of $\text{Cr}_{0.5}\text{Mo}_{0.5}\text{B}_2$. Frequency in units of THz and wave vector in units of $(1/\text{\AA})$. B atoms in green, Mo atoms in red and Cr atoms in blue. Data for the plots was obtained using the Phonopy software [63].

Table 3

Calculated elastic constants (C_{ij} in GPa) for the ternary systems $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ ($x = 0.25, 0.33, 0.50, 0.67, 0.75$) and binary systems CrB_2 , $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$.

Stoich.	x	System	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{14}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
CrB_2	0.00	Hexagonal	544	544	448	166	166	203	137	94						
Cr_3MoB_8	0.25	Monoclinic	572	569	649	226	221	213	131	130		-11	132	11	3	11
Cr_2MoB_6	0.33	Trigonal	587	581	664	229	229	230	125	125	9					
CrMoB_4	0.50	Trigonal	603	603	648	229	229	239	125	146	14					
CrMo_2B_6	0.67	Trigonal	581	568	613	231	231	226	121	171	15					
CrMo_3B_8	0.75	Monoclinic	573	573	658	222	226	222	124	144		0	147	0	0	0
$\alpha\text{-MoB}_2$	1.00	Hexagonal	602	602	423	170	170	230	143	209						
$\beta\text{-MoB}_2$	1.00	Trigonal	555	555	609	226	226	220	114	188	17					

Table 4

Calculated bulk modulus (B in GPa), Young's modulus (Y in GPa), shear modulus (G in GPa), Poisson's ratio (ν), vickers hardness (H_v and H_5 in GPa) and relative overall strength (Z) for the ternary systems $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ ($x = 0.25, 0.33, 0.50, 0.67, 0.75$) and binary systems CrB_2 , $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$.

Stoich.	x	B	Y	G	ν	H_v	H_5	Z
CrB_2	0.00	241	445	187	0.19	17.0	20.7	0.82
Cr_3MoB_8	0.25	286	534	225	0.19	24.5	25.0	1.03
Cr_2MoB_6	0.33	286	552	234	0.18	26.5	26.0	1.07
CrMoB_4	0.50	298	558	235	0.19	26.6	26.1	1.08
CrMo_2B_6	0.67	297	537	224	0.20	24.4	24.9	1.04
CrMo_3B_8	0.75	292	539	226	0.19	24.8	25.1	1.04
$\alpha\text{-MoB}_2$	1.00	304	451	180	0.25	15.8	20.0	0.85
$\beta\text{-MoB}_2$	1.00	298	520	215	0.21	22.7	23.9	1.00

six eigenvalues of the elastic tensor were calculated in each case. All the values are positive, confirming the mechanical stability of all the structures.

The bulk modulus (B) measures the resistance of a solid to compression and is an indicator of elastic strength. A strong correlation between the bulk modulus and valence electron density has been demonstrated, since more electrons in a given volume will result in higher repulsion forces

contributing to a higher bulk modulus [33]. The calculated bulk modulus for the binary CrB_2 is 241 GPa: it exhibits a strong variation in the z-direction and is much more uniform in the x and y-direction. The spatial dependence of the mechanical properties for all the studied crystal structures can be consulted in the supplementary information. With the addition of Mo, regardless of the concentration, the bulk modulus is automatically strengthened in plane. As observed in Figure 4 when $x = 0.50$, the ternary maximizes its bulk modulus at 298 GPa, the same value as $\beta\text{-MoB}_2$. However, the ternary is a much stronger material, because unlike $\beta\text{-MoB}_2$ (anisotropy $A = 1.44$), the bulk modulus is practically isotropic ($A = 1.15$).

The anisotropy A_X of each elastic modulus X is calculated by ELATE [17] according to the following relation:

$$A_X = \begin{cases} X_{\max}/X_{\min} & \text{if } \text{sign}(X_{\max}) = \text{sign}(X_{\min}) \\ \infty & \text{otherwise.} \end{cases} \quad (1)$$

Young modulus (Y) is a measure of the stiffness of a material under elastic deformation [10]. This parameter increases with the percentage of Mo until it reaches its maximum value of 558 GPa when the concentration is 50%. This value is 7% greater when compared to that of $\beta\text{-MoB}_2$. All the ternary systems in our investigation are close to be elastically isotropic,

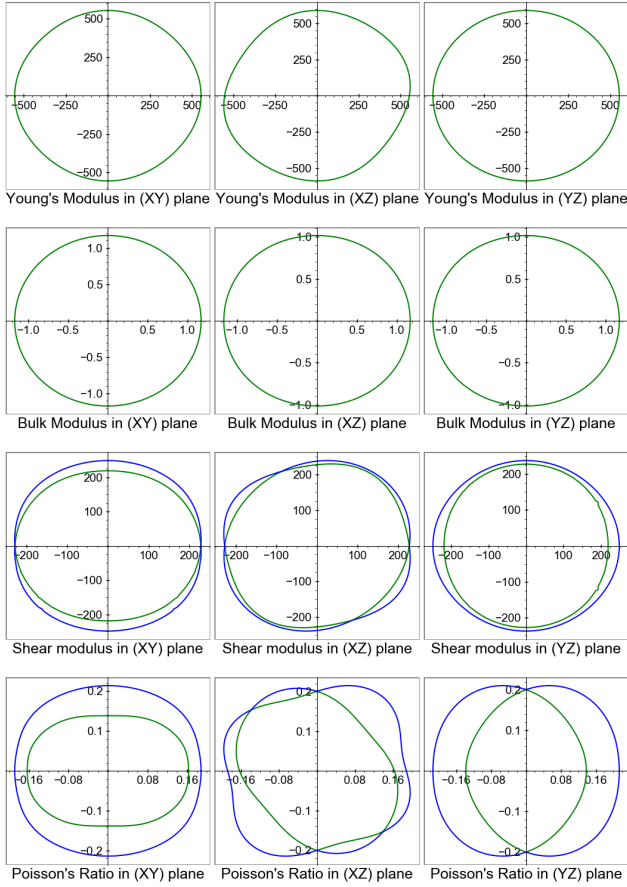


Figure 4: Spatial dependence of the calculated Young modulus, Bulk modulus, Shear modulus and Poisson ratio of $B_2Cr_{0.5}Mo_{0.5}$ trigonal crystal system. Green (blue) lines represent the minimum (maximum) positive values of each property. Plots were generated using the MechElastic package [58, 57]

and the anisotropy is minimized when $x = 50\%$ ($A = 1.12$).

Shear modulus (G) is a measure of the rigidity of a material to shear stress [10]. The addition of Mo enhances the transverse rupture strength of these compounds. For any concentration, the computed shear modulus is superior to those of the binary compounds, reaching its maximum value of 235 GPa for a 50% concentration. Similarly to the other moduli, the shear for the ternary systems is isotropic, and has the lowest anisotropy when $x = 50\%$ ($A = 1.14$).

The Poisson ratio (ν) defines the relationship between lateral and axial strain resulting from an applied axial stress [10]. As observed in Table 4, ν is very similar for all the studied structures, however, a full 3D analysis reveals certain differences. This parameter exhibits a great anisotropy for the binary systems ($A > 2.3$). For a 50% concentration, this anisotropy is significantly reduced ($A = 1.69$), as above making this compound the most uniform. For this concentration, the average value of the Poisson ratio is 0.19 with a maximum variation of 27%. This parameter presents its maximum value along the x and z-axis, and has a slightly lower value along the y-axis.

Mechanical properties such as B , Y , G and ν describe the

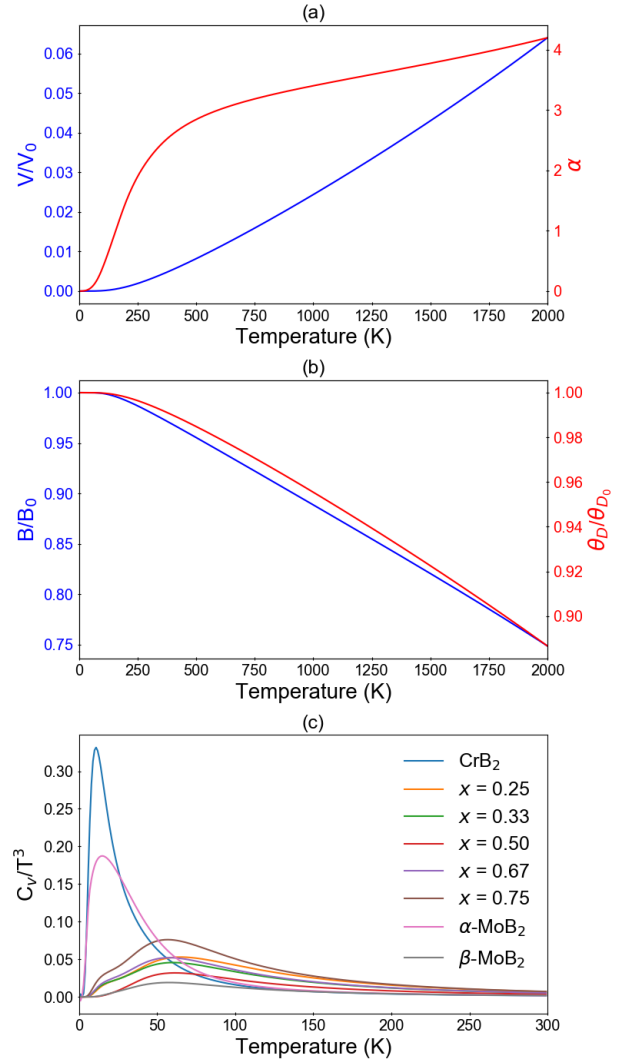


Figure 5: Average behaviour of (a) Volume (V/V_0) and Linear Coefficient of Thermal Expansion ($\alpha \times 10^{-5}/K$), (b) Bulk Modulus (B/B_0) and Debye Temperature (θ_D/θ_{D_0}) as a function of temperature using the Gibbs2 code [51]. (c) Temperature-dependence of (C_v/T^3 in $mJ/mol K^4$) for the ternary systems $Cr_{1-x}Mo_xB_2$ ($x = 0.25, 0.33, 0.50, 0.67, 0.75$) and binary systems CrB_2 , $\alpha-MoB_2$ and $\beta-MoB_2$ using the Phonopy software [63].

elastic behavior of a solid. But to fully describe the strength of a material, it is necessary to consider the plastic behavior as well. The hardness is one of the best known ways to measure the plastic strength of a solid [33]. However, determining the hardness is no easy task (experimentally or theoretically), so several semi-empirical relations have been established between the hardness and elastic parameters such as B , Y , G and ν [22]. The bulk modulus has been used as a predictor of hardness, but it has been proven that the shear modulus provides a much better correlation [33]. While B depends mostly on the valence electron density, G considers the nature and direction of the atomic bonds. Hence, covalent materials will have higher shear modulus than metals,

even though they may have similar bulk moduli [33].

Hardness for the binary systems was calculated using six different semi-empirical relations as described by Ivanovskii [22] and as implemented in the MechElastic package [58, 57]. The results were compared to experimental data in order to choose the method that best fits our systems (see supplemental information). The best results were obtained with the relation

$$H_5 = \frac{(1 - 2\nu)B}{6(1 + \nu)} \quad (2)$$

as proposed by Miao et al. [37]. As observed in Table 4 the predicted hardness (H_5) was considerably overestimated for the hexagonal binaries (CrB_2 and $\alpha\text{-MoB}_2$). However, the result for $\beta\text{-MoB}_2$ was very accurate. Given the similarities in the crystal structure of $\beta\text{-MoB}_2$ and the ternary systems, the hardness was estimated using this method.

Since the previous method (H_5), does not use the shear modulus to estimate the hardness, we performed a linear regression by including all 6 known experimental values, to establish a relationship between the experimental hardness and the shear modulus of the binary systems. The following relationship was obtained and extrapolated to calculate the hardness of the new compounds (H_v) as a function of the shear modulus.

$$H_v = 0.1978G - 19.877 \quad (3)$$

As shown in Table 4, both methods, H_v and H_5 , present similar results for the ternary systems, with a difference smaller than 1 GPa. In summary, $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ are hard alloys, with Vickers hardness greater than 24 GPa. The hardness is maximized when $x = 0.50$, reaching 26.6 GPa.

The relative overall strength (Z) with respect to $\beta\text{-MoB}_2$ was calculated and presented in Table 4. We chose $\beta\text{-MoB}_2$ as a reference point, because it is the stronger material among the binary systems. Z was calculated equally weighting B , Y , G and H_v . If ($Z > 1$), then the compound is stronger than $\beta\text{-MoB}_2$. As displayed in Table 4 the mechanical strength of $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ is maximized when $x = 0.50$.

A strong material needs to have a high bulk and Young modulus. Nevertheless, for practical applications, it is also desirable to have a high transverse rupture strength and hardness. We can observe that our compound $\text{Cr}_{0.5}\text{Mo}_{0.5}\text{B}_2$ exhibits excellent mechanical properties, surpassing those of $\beta\text{-MoB}_2$ and at a lower cost, considering Cr is cheaper than Mo [66].

3.2.2. Thermal properties

TMBs are exploited for their excellent high temperatures mechanical properties. We study the thermal properties of these alloys using the quasi-harmonic Debye model as implemented in the Gibbs2 code [51]. Figure 5 illustrates the temperature-dependence of the volume, bulk modulus, Debye temperature and linear coefficient of thermal expansion, up to 2000 K. Since the individual curves for the compounds are very similar to each other, the average behaviour is presented and the detailed data for each stoichiometry may be

Table 5

Normalized volume for a 3-atom cell with composition of $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ (V in $\text{\AA}^3$) at 0 K, density (ρ in kg/m^3) at 0 K, Debye temperature (θ_D in K) at 0 K, specific heat capacity at room temperature (C_v^{300K} in J/kg K) and maximum value at high temperatures (C_v^{max} in J/kg K), longitudinal sound velocity (u_L in m/s) and transverse sound velocity (u_T in m/s) for the ternary systems $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ ($x = 0.25, 0.33, 0.50, 0.67, 0.75$) and binary systems CrB_2 , $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$.

Stoich.	x	V_0	ρ	θ_D	C_v^{300K}	C_v^{max}	u_L	u_T
CrB_2	0.00	22.86	5347	941	591	934	9571	5907
Cr_3MoB_8	0.25	24.61	5708	888	546	869	10125	6272
Cr_2MoB_6	0.33	24.90	5887	876	526	833	10085	6310
CrMoB_4	0.50	25.58	6205	850	490	767	9926	6151
CrMo_2B_6	0.67	26.26	6508	826	460	711	9564	5865
CrMo_3B_8	0.75	26.67	6637	813	449	686	9453	5836
$\alpha\text{-MoB}_2$	1.00	26.45	7381	783	408	597	8584	4941
$\beta\text{-MoB}_2$	1.00	27.59	7076	786	409	621	9093	5513

consulted in the supplemental information. The phonopy code [63] was used to calculate the specific heat capacity.

Figure 5 (a) shows the average change of volume as a function of temperature. The absolute volume is larger in proportion to the concentration of Mo, which is normal as the Mo atoms are bigger than Cr atoms. The volume of all the structures increases monotonically with temperature (no anomalous thermal expansion). Also, our study reveals that when heated, the change in volume (ΔV) will be higher for Cr-rich compounds (see supplemental information). The normalized volume for each one of the structures is presented in Table 5.

In Figure 5 (a) is possible to appreciate the behavior of the linear coefficient of thermal expansion (α) for this family of diborides. Below room temperature (0 - 300 K), α follows approximately the same curve for all the compounds. At room temperature, the average value for the coefficient of thermal expansion is $2.2 \times 10^{-5}/\text{K}$. As the temperature continues to increase, the structures with less Mo will have higher values of α (see supplemental information). The thermal expansion is a consequence of the increase in phonon population with temperature and the anharmonic nature of the interatomic well. From the previous results, we can conclude that the Mo-B bonds should be stronger than Cr-B bonds, making it harder to expand the structure as the percentage of Mo increases.

Figure 5 (b) illustrates how the bulk modulus decreases as the temperature increases. There is no straight correlation between the percentage of Mo and the change of the bulk modulus with temperature. Nevertheless, it is observed that at high temperatures (>400 K) the bulk modulus decreases less for the monoclinic structures. The low symmetry of the crystal structures in these concentrations contributes to a smaller change in the bulk modulus with temperature (see supplemental information).

As shown in Figure 5 (b), the Debye temperature (Θ_D) decreases slightly as a function of temperature for all the

compounds, which have the same behaviour within a difference of 0.2%. This is a direct consequence of the interatomic separation increase with temperature, that will reduce the maximum Debye vibration frequency, and hence the Debye temperature. As presented in Table 5 the highest Θ_D (at 0 K) is presented by the hexagonal CrB_2 structure, which fits the intuition that stiff and light materials will have higher Θ_D . This value is in excellent agreement with the experimental data (950 K) reported by other authors [7]. $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$ phases have the lowest Θ_D . The Debye temperature at (0 K) for $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ alloys exhibits a linear relation ($\theta_D = 931.32 - 153.87x$) with the percentage of Mo ($0 < x < 1$). The fit error is inferior to 0.5%. From this relation it is observed that θ_D will be higher for a lower percentage of Mo. The Debye temperature (and Debye frequency), is expected to decrease as the elements in the crystal structure get heavier.

Specific heat (C_v) is a measure of the amount of energy per unit mass a solid can absorb before increasing its temperature a certain amount. Normally the ionic specific heat increases drastically as temperature rises, reaching a stable value according to the Dulong–Petit law. Since the heat capacity reaches 95% of its maximum value at $T = \theta_D$ [54], the specific heat at high temperature was calculated using this method and the results are presented in Table 5. The high temperature specific heat for these alloys lies between the maximum and minimum values imposed by the binary systems, and its value will decrease as the Mo contribution increases. The C_v at room temperature (300 K) are also presented in Table 5. The room temperature value of C_v is approximately 65% of the calculated high temperature specific heat for all the compounds.

At low temperatures the specific heat is described by the following relationship:

$$C_v = \gamma T + \beta T^3 \quad (4)$$

where the first term corresponds to the linear contribution of the conduction electrons and the second term to crystal lattice vibrations. The phonon dominated specific heat follows a T^3 power law, that agrees beautifully with the textbook on theory of solids [54]. Figure 5 (c) presents the phonon contribution to the net specific heat. At temperatures close to zero the only contribution to the specific heat comes from acoustic phonons. The peaks in this plot indicate the temperature at which the optical phonons are activated. Noticeably, the hexagonal binary structures present early peaks around 12 K, due to low frequency planar modes. The rest of the structures deviate from the Debye behaviour at approximately 60 K. In general, for the ternary systems, the peak shifts to lower temperature as the concentration of Mo increases, corresponding to the decrease of θ_D .

The speed of sound waves varies in each material because it depends on the elastic properties and the mass of the constituent atoms in each case. The longitudinal (u_L) and transverse (u_T) sound velocities for each crystal were

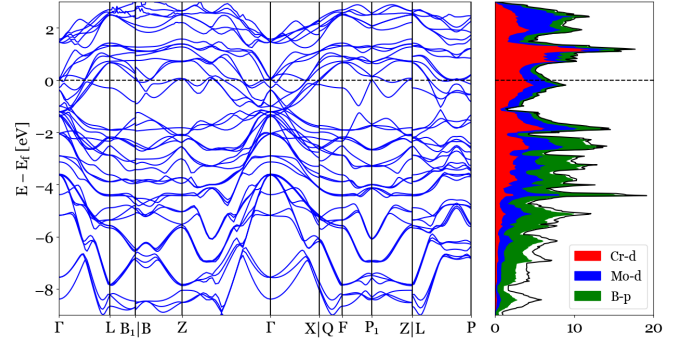


Figure 6: Total and projected density of states for $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ for $x = 0.50$ trigonal crystal system as a function of energy. The Fermi level is located at 0 eV. Plot generated using the PyProcar package [21].

calculated from the following relations [32]:

$$u_T = \sqrt{\frac{G}{\rho}} \quad (5)$$

$$q = \sqrt{\frac{1 - 2\nu}{2(1 - \nu)}} \quad (6)$$

$$u_L = \frac{u_T}{q} \quad (7)$$

where G is the shear modulus, ρ is the density, ν is the Poisson ratio and q is the ratio of transverse to longitudinal speed. The density of the compounds was calculated in terms of the cell volume and the molar mass of the atomic species. For the binary systems, the calculated densities are in good agreement with the experimental values of 5200, 7780 [55] and 7106 kg/m^3 [15] for CrB_2 , $\alpha\text{-MoB}_2$ and $\beta\text{-MoB}_2$ respectively. As observed in Table 5, the longitudinal velocity is always larger than the transverse one, with an average q value of 0.62 for the ternaries. The theory states that lighter and harder materials will have larger sound velocities. Consistently we found that $\text{Cr}_{0.75}\text{Mo}_{0.25}\text{B}_2$ presents the highest sound velocity among the studied compounds. In this case, a small inclusion of Mo atoms is enough to significantly strengthen the compound, yet keeping a low density in comparison with the other ternaries.

3.2.3. Electronic and Magnetic Properties

Due to the presence of TM in $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$, all systems in this study are metallic with occupied states at the Fermi level. Spin polarized SCAN calculations were performed to evaluate the magnetism in the ternary systems. No magnetism was conclusively observed for $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ for $x > 0$: The inclusion of Mo in the structures annihilates the magnetic behaviour observed in CrB_2 .

In Figure 6, we show the band structure and projected density of states (DOS) for the trigonal $\text{Cr}_{0.50}\text{Mo}_{0.50}\text{B}_2$. The DOS for the rest of the structures are presented in the supplemental information, since they are very similar to Figure

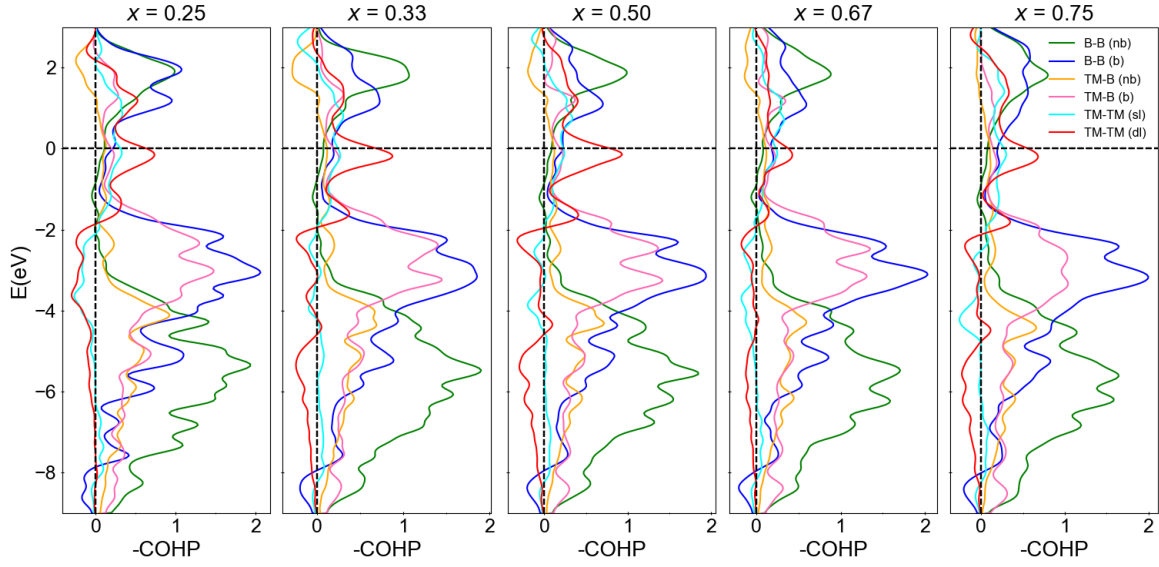


Figure 7: Crystal orbital Hamilton populations (COHP) curves of B-B interactions in buckled (b) and non-buckled (nb) B-layers, TM-B interactions with buckled B-layers (b) and non-buckled B-layers (nb), and TM-TM interactions among atoms in the same layer (sl) and different layers (dl) in the crystal structures for $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ ($x = 0.25, 0.33, 0.50, 0.67, 0.75$) using LOBSTER program [35]. Fermi level lies at zero eV. Bonding interactions are positive, anti-bonding interactions are negative.

6. As observed, the semi-core states are located below -9 eV and are mainly composed of B-s states for all the compounds. Closer to the Fermi level, the valence band is dominated by the Cr and Mo d-orbitals. Approximately 90% of the valence states correspond to transition metal hybrid d-orbitals, the rest is composed of a small contribution of the B-p states. As the percentage of Mo increases, the amount of Mo-d states increases as well, dominating the Fermi level, starting from 14% when $x = 0.25$ until a maximum of 57% for $x = 0.75$. The conduction bands have the same structure as the valence bands near the Fermi level.

The orbital symmetries do display some interesting behaviour as the % of Mo increases. For structures with $x = 0.25, 0.33, 0.67, 0.75$, there is a balanced contribution of different orbitals to the Fermi level. For these structures the Cr contribution of d_{xy} , d_{xz} , d_{yz} and $d_{x^2-y^2}$ orbitals is very similar. Alike, Mo-orbitals d_{xz} and d_{yz} and B-orbitals p_x and p_y display the same trend. In contrast with the other stoichiometries, $\text{Cr}_{0.5}\text{Mo}_{0.5}\text{B}_2$ has a different behavior: Cr and Mo $d_{x^2-y^2}$ and d_{yz} dominate the Fermi level with a small contribution of B p_y .

Figure 7 shows crystal orbital Hamilton populations (COHP) curves of B-B, TM-B and TM-TM interactions in $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$, produced using the LOBSTER program [35]. The strength of these compounds relies on the covalent B-B bonds similar to $\beta\text{-MoB}_2$. While non-buckled (nb) B-B layers have their maximum bonding at low energies (-5.49 eV), similar to CrB_2 and $\alpha\text{-MoB}_2$, the B-B buckled (b) layers display their strongest bonding contributions at higher energies (-3.26 eV). The inclusion of Mo automatically creates B-B buckled layers within the structures, increasing the overall strength of the ternary compounds. While the B-B layers across the solid contribute to elastic strength in the x and

y-direction, the covalent TM-B bonds support the material in the z-direction. All these ternaries exhibit the strongest density of TM-B bonding orbitals at approximately -3.05 eV and -4.30 eV below the Fermi level. At lower energies TM atoms bond strongly with B atoms in non-buckled layers, while at higher energies the bonding occurs between TM and B atoms in buckled layers. At the Fermi level, B-Mo bonding character is higher than the B-Cr, confirming that the Mo-B bonds are stronger than Cr-B bonds, as suggested by the behaviour of the coefficient of thermal expansion (α) in the previous section. Contrary to B-B and TM-B bonds, which display their maximum bonding at low energies, TM-TM exhibit their maximum bonding at the Fermi level and very weak bonding and/or anti-bonding behaviour at lower energies. TM-TM bonds between atoms in the same layer (sl) in the crystal structure, always have a positive, but very small bonding character at the Fermi level. In this case, the stronger bonds are Cr-Cr followed by Cr-Mo and Mo-Mo. On the other hand, TM-TM bonds between atoms in different layers (dl) exhibit a massive bonding character at the Fermi level. The stronger bonds are between Cr-Mo, followed by Cr-Cr and Mo-Mo. The strength of a metallic bond depends on the interatomic separation and the atomic valence. As the interatomic separation decreases and the number of delocalized valence electrons increases, the bond becomes stronger [50]. The superior strength of TM-TM bonds in different layers (along z-axis) over the TM-TM bonds in the same layer, results from a larger number of delocalized valence electrons. When the TM atoms are in different layers, they acquire electrons from the Boron layer in between them, contributing to the total number of delocalized valence electrons. Furthermore, it is well known that metallic bonds including TM display high binding from the in-

ner d-electron shells [26]. Consequently, the interlayer Cr-Mo bond is stronger than Cr-Cr due to a better overlap between 4d-orbitals (Mo) than between 3d-orbitals (Cr) [4]. Differently, the interlayer Cr-Mo bond is stronger than Mo-Mo given that at higher concentrations ($x = 0.67, 0.75$) the interatomic distance becomes large enough to weaken the Mo-Mo bond.

Even though all structures contain interlayer Cr-Mo bonds, due to their spatial configuration, structures with a concentration of $x = 0.25, 0.33, 0.67$ and 0.75 also contain Cr-Cr or Mo-Mo bonds. Some of these bonds are not as strong as the Cr-Mo bonds, relatively weakening the structures. Given the symmetry of $\text{Cr}_{0.5}\text{Mo}_{0.5}\text{B}_2$, this structure does not contain weak Cr-Cr or Mo-Mo bonds. The enhanced strength of the compound when $x = 0.50$ can be understood as a consequence of the high density of strong Cr-Mo bonds in between the Boron layers, and the absence of weaker Cr-Cr and Mo-Mo bonds.

4. Conclusion

In conclusion, the ternary system $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ was explored, and the ground state for each one of the studied concentrations was defined from first-principles calculations. The new structures are found to be either monoclinic or trigonal. They all display alternating planar and buckled layers of boron, similar to the binary boride end members. The monoclinic phases ($x = 0.25, 0.75$) have some layers shared by Cr and Mo atoms. On the other hand, the trigonal structures ($x = 0.33, 0.50, 0.67$) always have independent layers of Cr and Mo. The thermodynamical, dynamical, and mechanical stability of the compounds was verified. The mechanical properties such as bulk modulus (B), Young's modulus (Y), shear modulus (G), and Poisson's ratio (ν) were calculated from the elastic tensor in each case. The hardness (H_v) was computed from the derived mechanical properties, finding that the new compounds are hard alloys with Vickers hardness greater than 24 GPa. The results show that the mechanical strength of $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$ is maximized when $x = 0.50$. At this concentration the compound exhibits excellent mechanical properties, surpassing those of $\beta\text{-MoB}_2$ and at a lower cost. The temperature dependence of the volume (V), bulk modulus (B), Debye temperature (Θ_D), specific heat (C_v), and coefficient of thermal expansion (α), were also studied. All the systems in this study are metallic with occupied states at the Fermi level. For all the ternaries, the valence band is dominated by Cr and Mo hybrid d-orbitals with a small contribution of the B-p states. No magnetism was observed for $\text{Cr}_{1-x}\text{Mo}_x\text{B}_2$. COHP curves of B-B, TM-B and TM-TM interactions reveal that the superior strength of the new compounds is a consequence of the covalent B-B and TM-B bonds. The B-B layers contribute to strength in the x and y-direction, while the TM-B bonds support the structures in the z-direction. The enhanced strength when $x = 0.50$ is a consequence of the higher density of strong interlayer Cr-Mo metallic bonds at the Fermi level.

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