



## Editor's Choice

# First-principles investigation on the chemical bonding, elastic properties and ideal strengths of MoAlB and WAIB nanolaminated MAB phases



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## ABSTRACT

The present work deals with first-principles calculations on chemical bonding characteristics, elastic properties, and ideal strengths under both shear and tensile deformations of MoAlB and WAIB nanolaminated MAB phases. Diverse chemical bonds were found in MoAlB and WAIB, including strong B–B covalent bonds, Al–B covalent-ionic bonds, Mo–B bonds and metallic Mo–Al and Al–Al bonds. Elastic properties of MoAlB and WAIB are not highly anisotropic with shear modulus of (0 1 0)[1 0 0], (0 1 0)[0 0 1], (0 0 1)[1 0 0] similar to each other. Nevertheless, ideal strengths display significant anisotropy. The results show that ideal shear strength  $\tau_m$  of basal plane shears are lower than those of non-basal plane shears, while ideal tensile strength  $\sigma_m$  of the basal plane is lower than those of non-basal planes. In addition, ideal tensile strength of the basal plane is also much lower than ideal shear strengths of basal plane shears. The basal plane cleavage and shear failure both take place along the weakly bonded Al–Al layers. Moreover, the basal plane shear failure is found accompanied by remarkable expansion of the Al–Al layers, which reduces the resistance against basal plane shears. It suggests that MoAlB and WAIB tend to cleavage along the Al–Al layer or dislocations tend to multiply and slip in the Al–Al layer, which is similar to MAX phases.

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## 1. Introduction

Compounds with nanolaminated crystal structure have been widely investigated due to their fascinating properties, which make them promising candidates as damage tolerant ceramics [1–4], reinforcements for metals and ceramics [5], lithium ion conductors [6], self-lubricating materials [7]. As a distinctive family of nanolaminated compounds, MAX phases ( $M_{n+1}AX_n$ , M is an early transition metal, A is a III<sub>A</sub>–VI<sub>A</sub> group element, X is carbon or nitrogen) display both ceramic-like and metallic properties [1,3], which are underpinned by their nanolaminated crystal structure and diverse chemical bonding characteristics. Inspired by the successes of MAX phases, searching for compounds with similar structural features has attracted great research interest. Recently, a new family of nanolaminated compounds, MAB phases (M is a transition metal, A is a III<sub>A</sub> or IV<sub>A</sub> group element, B is boron), including  $(CrB_2)_nCrAl$  ( $n = 1, 2, 3$ ),  $Mn_2AlB_2$ ,  $Fe_2AlB_2$ ,  $MoAlB$  and  $WAIB$ , were synthesized and characterized [8–11]. In analogous to MAX phases, these MAB phases are structured with variable hard boride nano-layers interleaved with Al layers [8–11], which were confirmed by direct

observation using Z-contrast high resolution transmission electron microscopy by Lu et al. [11]. Systematic property measurements, including mechanical, thermal and oxidation properties, were conducted on MoAlB by Kota et al. [9], which reveal that MoAlB exhibits MAX-phase-like properties, such as low hardness (10.6 GPa), good electrical and thermal conductivities, and excellent oxidation resistance due to the formation of protective alumina scale [9]. This result is quite intriguing, since it is the first reported transition metal boride that is resistant to oxidation, which suggests that MAB phases are potentially useful in high temperature applications.

For a deep understanding of MAB phases, it is essential to study their chemical bonding characteristics and fundamental mechanical properties by first principles calculations. According to structural differences, MAB phases can be divided into two groups. In the first group, including  $(CrB_2)_nCrAl$  ( $n = 1, 2, 3$ ),  $Mn_2AlB_2$  and  $Fe_2AlB_2$ ,  $M_{n+1}B_{2n}$  nano-layers are interleaved by a single layer of Al. In the second group, including MoAlB and WAIB, two layers of Al are inserted between MB nano-layers. For  $(CrB_2)_nCrAl$  ( $n = 1, 2, 3$ ), theoretical investigations have clarified their bonding nature [12,13], anisotropic elastic properties [13], and their preferred failure models [14]. For MoAlB, its chemical bonding characteristics, elastic constants and lattice dynamics have been calculated [15–17]. However, details on the bonding nature and the anisotropy

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in elastic properties have not been well verified, and the preferred failure models have not been studied. In the present study, these unsolved problems of both MoAlB and WAIB were investigated by first-principles calculations. To verify preferred failure models, ideal strengths under different deformation models were calculated. Ideal strength of a material can be defined as the minimum stress required to induce permanent deformation (e.g. dislocations or cracks) in a perfect crystal [18,19]. Though it is difficult to obtain ideal strengths from experiments, first-principles methods provide a good choice to evaluate ideal strengths and to explore the microscopic nature that controlling ideal strengths [14,20–22].

## 2. Calculation methods

First principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) code [23]. In the calculations, Vanderbilt-type ultrasoft pseudopotentials were used to model the interactions between electrons and ion cores [24]. The exchange-correlation was treated by the Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) [25]. The plane wave basis set cutoff energy was set to be 400 eV, and  $k$ -points mesh with a separation of  $0.04 \text{ \AA}^{-1}$  according to Monkhorst-Pack method [26] was adopted in the Brillouin zone. Lattice parameters were modified to minimize the enthalpy and interatomic forces. Elastic stiffness was determined from a linear fit of the calculated stress as a function of strain. To evaluate ideal strengths, stress-strain responses were simulated by incrementally increasing the applied stress under a given deformation model. At each step, the imposed stress was increased by a fixed value and the crystal cell was fully relaxed until all other stress components vanished. Then, the relaxed cell was taken as the starting structure for the next step. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [27] was used in geometry optimization. The convergence criteria for optimizations were set as follows: the difference in total energy within  $1 \times 10^{-6}$  eV/atom, the maximum ionic Hellmann-Feynman force within  $0.002 \text{ eV/\AA}$ , the maximum ionic displacement within  $1 \times 10^{-4} \text{ \AA}$ , and maximum stress difference within  $0.02 \text{ GPa}$ .

## 3. Results and discussions

### 3.1. Crystal structure and bonding nature

Fig. 1a illustrates a  $2 \times 1 \times 2$  crystal cell of MoAlB with its  $[001]$  and  $[100]$  view shown in Fig. 1b and c, respectively. MoAlB and WAIB are crystallized with the space group  $Cmcm$  [8]. Mo(W), Al, B atoms all occupy  $4c(0, y, 0.25)$  Wyckoff positions. The geometrical optimized lattice constants and  $x$  values for Mo(W), Al and B are listed in Table 1, which agree well with experimental measurements [8] and calculations by other investigators [16,17], indicating the reliability of our calculations. The crystal structure of Mo(W)AlB consists of hard boride Mo(W)B nano-layers interleaved with two Al layers, which forms a nanolaminated structure as shown in Fig. 1. The direction perpendicular to these nano-layers is defined as the  $b$  direction of the unit cell. B atoms form linear zig-zag chains with the chain direction parallel to the  $c$  direction of the unit cell. The two Al layers and the adjacent two Mo(W) layers (with one above and the other below the Al layers) constitute a BCC-like structure, if negating the atom type difference. Then,  $a$  axis and  $c$  axis of the unit cell resemble  $\langle 100 \rangle$  axis of the BCC-like structure, where  $a = 3.216 \text{ \AA}$  and  $c = 3.103 \text{ \AA}$  of MoAlB are similar to the lattice parameter  $3.157 \text{ \AA}$  of BCC-Mo,  $a = 3.222 \text{ \AA}$  and  $c = 3.114 \text{ \AA}$  of WAIB are similar to the lattice parameter  $3.165 \text{ \AA}$  of BCC-W.

To analyze the bonding characteristics in Mo(W)AlB, band structure, electron density of state (DOS), and electron density

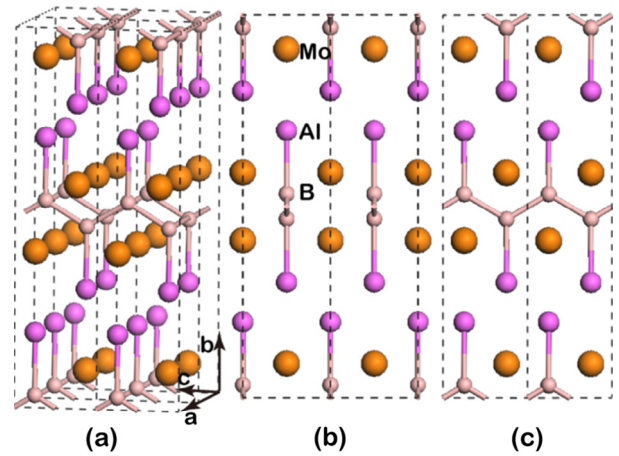


Fig. 1. (a)  $2 \times 1 \times 2$  crystal cell of MoAlB; (b)  $[001]$  view and (c)  $[100]$  view of the crystal cell in (a).

distribution maps correlated to different bands are shown in Fig. 2. In Fig. 2a, the filled energy bands are roughly divided into three groups, which are colored in red<sup>1</sup>, green, and blue, respectively. For the first group with energy below  $-5 \text{ eV}$  (red bands), the electrons are mainly contributed from  $s$  and  $p$  electrons of B and Al, which can be seen from Fig. 2b. It indicates strong bonds formed between B–B and B–Al. Fig. 2d displays electron density distribution map correlated to the red bands on  $(200)$  plane (the red plane in Fig. 2c), which clearly shows strong B–B  $\sigma$  bonds and Al–B covalent-ion bonds formed in this range of energy. The energy range of the second group (green bands) is  $-5 \text{ eV} \sim -2.5 \text{ eV}$ , which are mainly contributed from Mo- $d$ , Al- $p$  and B- $p$  electrons, as can be seen from Fig. 2b. Electron density distribution map correlated to the green bands on  $(002)$  plane (the green plane in Fig. 2c) are shown in Fig. 2e, where the bonding between B- $p$  electrons and Mo- $d$  electrons are evident. For the last group with energy higher than  $-2.5 \text{ eV}$  (blue bands), the electrons are mainly contributed from Mo- $d$  and Al- $p$  electrons, which are metallic bonds. Electron density distribution map correlated to the blue bands in one of the  $\{110\}$  planes of the BCC-like region (the blue plane in Fig. 2c) are shown in Fig. 2f, which reveals that metallic bonding between Al–Al are highly directional.

### 3.2. Elastic properties

Elastic constants of MoAlB and WAIB were calculated and listed in Table 2, where values of MoB and WB were also calculated for comparison. For easy of comparison, elastic constants of MoB and WB were reset by exchanging  $b$  axis and  $c$  axis, since the basal plane of MoAlB is  $(010)$  plane, while the basal plane of MoB is  $(001)$  plane. Values calculated in the present work agree well with those reported in Ref. [16,17], indicating the reliability of our calculations. For an orthorhombic system, Born criteria [28] regarding mechanical stability are as follows:

$$\begin{aligned} c_{11} > 0; \quad c_{44} > 0; \quad c_{55} > 0; \quad c_{66} > 0; \\ c_{11}c_{22} - c_{12}^2 > 0; \\ (c_{11}c_{22}c_{33} + 2c_{12}c_{23}c_{31}) - (c_{11}c_{23}^2 + c_{22}c_{31}^2 + c_{33}c_{12}^2) > 0 \end{aligned}$$

It is easy to check that both MoAlB and WAIB satisfy the Born mechanical stability criteria. In addition, phonon dispersions of MoAlB and WAIB were also calculated to check their stability, where no imaginary model was obtained, indicating the stability

<sup>1</sup> For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

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