The Electronic Structural and Elastic Properties of Mg$_{23}$Al$_{30}$ Intermediate Phase under High Pressure

Liang Sun $^{1,}$*, Weihua Hui $^{1}$, Yong Zhou $^{1}$, Wenyuan Zhai $^{1,}$*, Hui Dong $^{1}$, Yanming Liu $^{1}$, Qian Gao $^{1}$, Mohan Dang $^{1}$ and Jianhong Peng $^{2}$

$^{1}$ College of Material Science and Engineering, Xi’an Shiyou University, Xi’an 710065, China; weihuahui@xsyu.edu.cn (W.H.); zhouyong@xsyu.edu.cn (Y.Z.); donghui@xsyu.edu.cn (H.D.); liuyanming@xsyu.edu.cn (Y.L.); gaoqian@xsyu.edu.cn (Q.G.); Mohandang@xsyu.edu.cn (M.D.)

$^{2}$ College of Physics and Energy, Qinghai Nationalities University, Xining 810007, China; pengjianhong@xsyu.edu.cn

* Correspondence: lsun@xsyu.edu.cn (L.S.); 180606@xsyu.edu.cn (W.Z.)

Received: 2 June 2020; Accepted: 21 July 2020; Published: 25 July 2020

Abstract: Magnesium aluminum alloy has a broad potential utilization because of its high specific stiffness, specific strength, excellent anti-vibration performance and good impact resistance. The main reason for the weakness of the welding strength of magnesium/aluminum as dissimilar metals during the welding process is the Mg$_{23}$Al$_{30}$ intermetallic compound. In the present article, first principle calculation methods are introduced to study the thermodynamic properties, structural stability, electronic structure, elastic properties and performance of Mg$_{23}$Al$_{30}$ under pressure. The decreasing range of $c$ is greater than that of $a$, which indicates that the material has anisotropy. Mg and Al atoms in the Mg$_{23}$Al$_{30}$ structure are characterized by metal bonds. It can be concluded that Mg$_{23}$Al$_{30}$ not only behaves as a stable crystal structure but also has good elastic stability. After determined the ratio of the $G/B$ criterion, Mg$_{23}$Al$_{30}$ belongs to the ductile materials. When treated with pressure in the range of 0–6 GPa, the volume modulus $B$, Young’s modulus $E$ and shear modulus $G$ of Mg$_{23}$Al$_{30}$ materials all increase with the pressure, which show its excellent mechanical stability.

Keywords: electronic structural; elastic properties; intermediates

1. Introduction

With the rapid development of the application of lightweight structural materials, magnesium aluminum alloy has broad application potential in military, aircraft and automobile manufacturing and other fields, due to its high specific stiffness, specific strength and excellent vibration resistance [1–4]. The application of Mg-Al alloy depends on the particular stoichiometric and non-stoichiometric phase of mechanical properties of the metal, the most commonly affected chemically active elements of Mg [5]. It can be inferred from a previous theory [6] and other experimental studies [7] that the precipitated intermetallic compound Mg$_{17}$Al$_{12}$ can serve as a creep-deformed factor at high temperatures, thereby reducing the performance of the Mg-Al alloy.

At present, there are numerous studies on the connection of magnesium/aluminum as dissimilar materials, involving fusion welding, brazing, diffusion welding, friction stir welding, electron beam welding, TIG welding, laser welding, etc., but the obtained joint strength still struggles to meet the production needs. It is found that the main reason for limiting the welding strength of magnesium/aluminum as dissimilar metals is the production of Mg$_{23}$Al$_{30}$ intermetallic compounds during the welding process. Mohammadi [8] and Wang et al. [9] investigated the friction stir welding with AZ31 of magnesium alloy with 6061 aluminum alloy. The results showed that Mg$_{23}$Al$_{30}$ intermetallic compounds were systemically produced in the welding core area and could hardly
be handled. Ben et al. [10] and Liu Zhengjun et al. [11] used TIG welding in order to connect magnesium/aluminum as dissimilar alloys, while Mg$_{23}$Al$_{30}$ intermetallic compounds are found in the welded joint. Their concentration on the magnesium side was found, leading to the magnesium side being prone to fracture, while the interface near the aluminum side was well bound. Azizi [12] used vacuum diffusion welding to connect 7075 aluminum alloy and AZ31B magnesium alloy to improve joint performance by adjusting the welding temperature and welding time.

In addition, several previous calculations have studied the crystal structure and mechanical properties of the Mg-Al alloy mesophase. Several phases, like Mg$_{17}$Al$_{12}$, Mg$_{13}$Al$_{14}$ and MgAl$_2$, have been studied by Zhuang et al. [13] and they declared their elastic and thermodynamic properties. The lack of Mg$_{13}$Al$_{14}$ and MgAl$_2$ in the Mg-Al binary phase diagram is consistent with their positive formation energy. The electronic structure, elasticity and thermodynamic properties of Mg$_{17}$Al$_{12}$ were studied by Huang [14] and Hu et al. [15] using first principles studies, which finally concluded that Mg$_{17}$Al$_{12}$ has a high rigidity and good compressibility.

Based on the discussion above, an Mg$_{23}$Al$_{30}$ intermetallic compound was produced in the welding engineering area and it greatly affected the strength of Mg-Al alloy, which had a profoundly reduced shear strength and increased interface hardness. However, for Mg$_{23}$Al$_{30}$, its structural stability, thermodynamic properties, electronic structure, mechanical properties and even properties under pressure are rarely studied. Therefore, the physical properties of Mg$_{23}$Al$_{30}$ were systematically studied in this paper based on the change in pressure.

2. Calculation Methods and Theoretical Models

This paper utilizes a density functional theory based on first principles and uses the Cambridge series total energy package (CASTEP in Materials Studio) to theoretically calculate the electronic structure and elastic properties of Mg$_{23}$Al$_{30}$ [16–18]. The core orbit is described by the projector augment wave (PAW) [19] method. The exchange and correlation potential of the electron–electron interaction is corrected by the Perdew, Burke and Ernzerhof (PBE) [20] form in the generalized gradient approximation (GGA). In this process, the plane wave cut-off energy (Ecut) in this process is 400 eV. The selection of the k vector in the Brillouin zone is $3 \times 3 \times 3$, and the self-consistent precision is $1.0 \times 10^{-6}$ eV atom$^{-1}$. The Broyden, Flecher, Goldfarb and Shanno (BFGS) algorithm is applied to geometrically optimize the constructed model. The convergence standard of single atom energy is $1.0 \times 10^{-8}$ eV, the standard of the convergence of the internal stress of the crystal is 0.001 GPa. The convergence criterion for the maximum displacement of atoms is $1.0 \times 10^{-5}$ Å.

3. Results and Discussion

3.1. Crystal Structural Properties

Figure 1 shows the crystal structure model of the Mg$_{23}$Al$_{30}$ mesophase, which belongs to a trigonal crystal system, the ICSD ID is 57965 and the space group is No. 148, R$\bar{3}$. Besides, the calculated cell parameters and volumes with pressure are shown in Table 1, and the comparison with the experimental value.

![Figure 1. Crystal structure of Mg$_{23}$Al$_{30}$ at ground state.](image-url)
Table 1. The calculated parameters of Mg$_{23}$Al$_{30}$ under different pressures (pressure range: 1–8 GPa).

| Pressure | $a = b$ (Å) | $c$ (Å) | Volume (Å$^3$) | Density (g/cm$^3$) | $\Delta H$ (eV/atom) |
|----------|-------------|---------|----------------|-------------------|---------------------|
| 0 GPa    | 12.86       | 21.66   | 3100.07        | 2.20              | -0.035              |
| 1 GPa    | 12.88       | 21.23   | 3049.07        | 2.24              | -                   |
| 2 GPa    | 12.80       | 21.12   | 2999.14        | 2.27              | -                   |
| 3 GPa    | 12.73       | 21.03   | 2953.28        | 2.31              | -                   |
| 4 GPa    | 12.67       | 20.94   | 2910.58        | 2.34              | -                   |
| 5 GPa    | 12.61       | 20.86   | 2870.88        | 2.37              | -                   |
| 6 GPa    | 12.55       | 20.78   | 2833.45        | 2.41              | -                   |
| 7 GPa    | 12.49       | 20.70   | 2798.75        | 2.44              | -                   |
| 8 GPa    | 12.44       | 20.63   | 2765.49        | 2.47              | -                   |

First of all, the theoretical unit cell parameters obtained after the geometric optimization of Mg$_{23}$Al$_{30}$ are in good agreement with the experimental values, and also consistent with other calculation results, which can confirm the high reliability of our calculation results.

Second, the lattice constant and volume change trend of Mg$_{23}$Al$_{30}$ under different pressures are displayed in Figure 2. The ratio of $c/c_0$ and $V/V_0$ decreases with pressure. The ratio of $a/a_0$ decreases with increasing pressure. When the pressure is 8 GPa, the lattice parameters $a$ and $c$ are reduced by 3.27% and 4.70%, and the volume $V$ is reduced by 10.79%. This indicates that the increase in pressure caused the crystal to be compressed. The increase in the lattice parameter of the external pressure is gradually decreased, resulting in a unit cell volume decrease. It can be seen from Table 1, with the pressure increases, that the lattice constant of Mg$_{23}$Al$_{30}$ gradually decreases, and the volume $V_0$ also decreases.

3.2. Enthalpy of Formation

The thermodynamic stability of solid crystals can be judged by the enthalpy of formation ($\Delta H$) of the system [23]. When the value is negative, it represents a stable intermediate phase. The absolute value of the enthalpy of formation is taken. When the absolute value is larger, it is easier to form the intermetallic compound [24]. Equation (1) can calculate the formation enthalpy [25]:

$$\Delta H = \frac{1}{x+y} \left( E_{\text{tot}} - xE_{\text{solid}}^A - yE_{\text{solid}}^B \right)$$

(1)

In the formula, the total energy of the ground state of the crystal is expressed as $E_{\text{tot}}$. $x$ and $y$ refer to the numbers of Mg and Al atoms in the unit cells. The total energy of solid Mg and Al atoms is represented by $E_{\text{solid}}^A$ and $E_{\text{solid}}^B$, the data of Mg and Al atom calculations are $-973.901$ eV and...
−56.475 eV. Table 1 shows the calculated enthalpy of formation. The formation enthalpies (ΔH) of Mg$_{23}$Al$_{30}$ are negative when there is no pressure, which indicates that the mesophase of Mg$_{23}$Al$_{30}$ has thermodynamic stability with no pressure.

3.3. Electronic Structures

The electronic structure of the Mg$_{23}$Al$_{30}$ mesophase is studied in this section, which leads to a better understanding of its bonding structure. The electronic structure properties of the Mg$_{23}$Al$_{30}$ mesophase at 0 GPa, 4 GPa and 8 GPa pressures are shown in Figure 3. The band structure of the Mg$_{23}$Al$_{30}$ mesophase at 0 GPa, 4 GPa and 8 GPa are shown in Figure 3a,d,g, respectively. The Fermi levels are indicated by the dotted lines. Generally, the energy value of the Fermi level is 0 eV. It can be seen from the figure that multiple energy bands pass through the Fermi level and the bands are not obvious, and electrons can easily gain energy and associate with transitions to the conduction band and conduct electricity. It indicates that Mg$_{23}$Al$_{30}$ has a strong metallic character, as well as strong electro-conductivity. In Figure 3a,d,g, it can be seen that the energy distribution is asymmetric, and its conductivity exhibits a strong anisotropy. The total state density (DOS) of the Mg$_{23}$Al$_{30}$ mesophase at 0 GPa, 4 GPa and 8 GPa is depicted in Figure 3b,e,h. It can be seen from the figure that the peak of the total state density of the Mg$_{23}$Al$_{30}$ mesophase and the state density of the Fermi surface both decrease with increasing pressure, which indicates that the metal properties are reduced. Figure 3c,f,i show the partial state density (PDOS) of Mg$_{23}$Al$_{30}$ at 0 GPa, 4 GPa and 8 GPa, respectively. By analyzing the partition density map, the bonding among the atoms can be seen. The valence band of Mg$_{23}$Al$_{30}$ can be regarded as having three parts. In the region of −10~−6.5 eV, the 3s orbital of Al dominates, and the 3s and 3p orbitals of Mg contribute. In the region of −6.5~0 eV, the 3s and 3p orbitals of Al and 2p and 3s of Mg contribute simultaneously, among which the 3p orbitals of Al contribute the most. In the region of 0–2 eV, the 2p orbital of Mg and the 3p orbital of Al mainly contribute, while the 3s orbital of Mg and the 3s orbital of Al contribute less.

Additionally, Figure 4 shows the change in total state density under pressure. It can be seen from the figure that the trend of total state density (DOS) decreases from 0 GPa to 8 GPa. Then the structure of the Mg$_{23}$Al$_{30}$ mesophase from 0 GPa to 8 GPa is stable. However, with increasing pressure values, there is a slight decrease in the total density of states at the Fermi level of charge, which indicates that the metal is applied as the intermediate Mg$_{23}$Al$_{30}$ phase reduces in pressure.

The bond formation between atoms can get an objective result through Mulliken’s overall analysis. In the present paper, the Mulliken population analysis method is introduced to calculate the orbital population, total atomic population and charge values of Mg$_{23}$Al$_{30}$ under the conditions of 0 GPa, 4 GPa and 8 GPa, respectively, as shown in Table 2. It can be noted that the 3s orbital of Mg loses electrons, and the 2p orbital gains electrons; the 3s orbital of Al loses electrons, and the 3p orbital gains electrons. On the whole, Mg atoms lose electrons and become positively charged, while Al atoms gain electrons and become negatively charged. This result satisfies the law of atomic electronegativity. In addition, the electron transfer from individual atoms can be seen in Table 2. The more electrons that are transferred, the stronger the ionic bond interaction between the atoms. At 0 GPa, the amount of electrons transferred from Mg to Al is 3.24. At 4 GPa, the amount of electrons transferred from Mg to Al is 3.53. At 8 GPa, the amount of electrons transferred from Mg to Al is 3.77. It can be seen that the ionic bond interaction between Mg and Al becomes stronger as the pressure increases.
Figure 3. Calculated band structure: (a) at 0 GPa, (d) at 4 GPa, (g) at 8 GPa; total density of states: (b) at 0 GPa, (e) at 4 GPa, (h) at 8 GPa; partial density of states: (c) at 0 GPa, (f) at 4 GPa, (i) at 8 GPa; the Fermi level is indicated by the blue dotted line.
The bond formation between atoms can get an objective result through Mulliken’s overall analysis. In the present paper, the Mulliken population analysis method is introduced to calculate the orbital population, total atomic population and charge values of Mg$_{23}$Al$_{30}$ under the conditions of 0 GPa, 4 GPa and 8 GPa, respectively, as shown in Table 2. It can be noted that the $3s$ orbital of Mg loses electrons, and the $2p$ orbital gains electrons; the $3s$ orbital of Al loses electrons, and the $3p$ orbital gains electrons. On the whole, Mg atoms lose electrons and become positively charged, while Al atoms gain electrons and become negatively charged. This result satisfies the law of atomic electronegativity. In addition, the electron transfer from individual atoms can be seen in Table 2. The more electrons that are transferred, the stronger the ionic bond interaction between the atoms. At 0 GPa, the amount of electrons transferred from Mg to Al is 3.24. At 4 GPa, the amount of electrons transferred from Mg to Al is 3.53. At 8 GPa, the amount of electrons transferred from Mg to Al is 3.77. It can be seen that the ionic bond interaction between Mg and Al becomes stronger as the pressure increases.

Table 2. Mulliken population analysis of Mg$_{23}$Al$_{30}$ at 0 GPa, 4 GPa and 8 GPa.

| Pressure | Species | s   | p   | Total | Charge (e) |
|----------|---------|-----|-----|-------|------------|
| 0 GPa    | Mg      | 0.72| 6.62| 7.34  | 0.66       |
|          | Mg      | 0.74| 6.71| 7.46  | 0.54       |
|          | Mg      | 0.73| 6.83| 7.56  | 0.44       |
|          | Mg      | 0.87| 6.87| 7.74  | 0.26       |
|          | Mg      | 0.71| 6.69| 7.40  | 0.60       |
|          | Mg      | 0.68| 6.58| 7.26  | 0.74       |
|          | Al      | 1.19| 2.18| 3.37  | −0.37      |
|          | Al      | 1.23| 2.16| 3.40  | −0.40      |
|          | Al      | 1.23| 2.17| 3.40  | −0.40      |
|          | Al      | 1.25| 2.18| 3.43  | −0.43      |
|          | Al      | 1.31| 2.23| 3.54  | −0.54      |
| 4 GPa    | Mg      | 0.70| 6.59| 7.29  | 0.71       |
|          | Mg      | 0.73| 6.68| 7.41  | 0.59       |
|          | Mg      | 0.72| 6.81| 7.53  | 0.47       |
|          | Mg      | 0.86| 6.86| 7.71  | 0.29       |
|          | Mg      | 0.68| 6.65| 7.33  | 0.67       |
|          | Mg      | 0.65| 6.56| 7.20  | 0.80       |
|          | Al      | 1.17| 2.23| 3.40  | −0.40      |
|          | Al      | 1.21| 2.21| 3.43  | −0.43      |
|          | Al      | 1.21| 2.23| 3.44  | −0.44      |
|          | Al      | 1.22| 2.24| 3.46  | −0.46      |
|          | Al      | 1.29| 2.29| 3.58  | −0.58      |
| 8 GPa    | Mg      | 0.68| 6.57| 7.25  | 0.75       |
|          | Mg      | 0.71| 6.65| 7.36  | 0.64       |
|          | Mg      | 0.70| 6.80| 7.50  | 0.50       |
|          | Mg      | 0.84| 6.84| 7.68  | 0.32       |
|          | Mg      | 0.66| 6.62| 7.29  | 0.71       |
|          | Mg      | 0.63| 6.52| 7.15  | 0.85       |
|          | Al      | 1.16| 2.27| 3.43  | −0.43      |
|          | Al      | 1.20| 2.26| 3.46  | −0.46      |
|          | Al      | 1.19| 2.28| 3.47  | −0.47      |
|          | Al      | 1.21| 2.29| 3.50  | −0.50      |
|          | Al      | 1.28| 2.33| 3.61  | −0.61      |

In order to understand the bonding characteristic between atoms in Mg$_{23}$Al$_{30}$, the charge density distribution and differential charge density distribution of each cell (110) surface at 0 GPa, 4 GPa and 8 GPa were selected for analysis. The results are shown in Figure 5. Figure 5a–c show the charge...
density at 0 GPa, 4 GPa and 8 GPa. It can be seen from the figure that the charge density around the Al atoms is lower than that around the Mg atoms. In addition, when the pressure increases, the charge density also increases, which reflects that, as the pressure increases, the interaction force between the atoms also becomes stronger. The difference in charge density at 0 GPa, 4 GPa and 8 GPa is shown in Figure 5d–f, respectively. The strength, bonds and properties of the interactions between the atoms and the situation of the electrons gained and lost by each atom can be seen. Ionic bonds are the main type between Mg atoms and Al atoms. In the case of each atom, the electron mainly shows that the Mg atom loses some electrons and the Al atom gains some electrons. Additionally, the red region between adjacent Al atoms increases with increasing pressure, which indicates that the covalent bond becomes stronger with increasing pressure.

![Image of charge density maps](image_url)

**Figure 5.** Charge density distribution maps (a–c) of Mg23Al30 at 0 GPa, 4 GPa and 8 GPa, and differential charge density distribution maps (d–f).

### 3.4. Elastic Properties

The elastic constant of the crystal is very crucial and reflects the macro-mechanical properties of the material. The physical quantities of the material that are stretched and compressed within the elastic limit range are expressed by the elastic modulus. It is the most important and characteristic mechanical property of the elastic modulus along the longitudinal direction [26,27]. The Young’s modulus, shear modulus and Poisson’s ratio can further determine the properties of the material. To further understand the mechanical properties of Mg23Al30, a series of properties, such as elastic constant, elastic modulus and hardness from 0 GPa to 6 GPa, are analyzed and shown in Table 3.

As can be seen from Table 3, Mg23Al30 belongs to the trigonal crystal system, its elastic stability can be judged by the elastic stability criterion proposed by Born–Huang and it satisfies the following relation [13]:

\[
C_{11} > |C_{12}|, C_{44} > 0, (C_{11} + C_{12})C_{33} > 2C_{13}^2, (C_{11} - C_{12})C_{44} > 2C_{14}^2
\]  

(2)
It can be seen from Table 3 that the elastic constant of Mg$_{23}$Al$_{30}$ at 0 GPa conforms to the following relationship. It is also possible to satisfy other types of conditions (1) under pressure by calculating the elastic constant, which confirms that Mg$_{23}$Al$_{30}$ has a stable structure from 0 GPa to 6 GPa.

### Table 3. Elastic constants of Mg$_{23}$Al$_{30}$ under different pressures.

| Pressure (GPa) | $C_{11} = C_{22}$/GPa | $C_{12} = C_{23}$/GPa | $C_{13} = C_{23}$/GPa | $C_{33}$/GPa | $C_{44}$/GPa | $C_{66}$/GPa |
|---------------|------------------------|------------------------|------------------------|-------------|-------------|-------------|
| 0             | 78.49                  | 37.35                  | 44.93                  | 79.33       | 27.45       | 20.57       |
| 1             | 82.30 [28]             | 39.10                  | 33.59                  | 69.68       | 14.59       | -           |
| 2             | 84.29                  | 40.79                  | 48.49                  | 85.27       | 29.25       | 21.75       |
| 3             | 89.35                  | 43.92                  | 52.74                  | 90.96       | 30.83       | 22.71       |
| 4             | 95.39                  | 47.25                  | 55.41                  | 96.59       | 32.85       | 24.07       |
| 5             | 100.65                 | 50.34                  | 58.78                  | 103.55      | 34.39       | 25.15       |
| 6             | 105.89                 | 53.74                  | 65.22                  | 113.66      | 38.01       | 27.65       |

In this paper, the Vogit–Reuss–Hill method [28] is used to approximate the bulk modulus, Young’s modulus, shear modulus and Poisson’s ratio of the Mg$_{23}$Al$_{30}$ mesophase from 0 GPa to 8 GPa. The results are listed in Table 4. The material’s ability to resist compressive deformation can be expressed by the bulk modulus $B$ [29]. The shear modulus $G$ reflects the material’s ability to resist plastic deformation [30]. Young’s modulus $E$ can reflect the material’s ability to resist elastic deformation [31].

### Table 4. Elasticity, modulus, Poisson’s ratio and hardness of Mg$_{23}$Al$_{30}$ under different pressures.

| Pressure (GPa) | $B$/GPa | $G$/GPa | $G/B$ | $E$/GPa | $\nu$ | $H_V$/GPa |
|---------------|---------|---------|-------|---------|-------|-----------|
| 0             | 51.06   | 24.45   | 0.48  | 63.26   | 0.29  | 3.43      |
| 1             | 55.29   | 25.98   | 0.47  | 67.38   | 0.30  | 3.45      |
| 2             | 59.06   | 27.28   | 0.46  | 70.92   | 0.30  | 3.64      |
| 3             | 63.30   | 29.00   | 0.46  | 75.48   | 0.30  | 3.87      |
| 4             | 67.11   | 30.34   | 0.45  | 79.10   | 0.30  | 4.06      |
| 5             | 71.12   | 31.67   | 0.45  | 82.74   | 0.31  | 4.09      |
| 6             | 74.71   | 33.46   | 0.45  | 87.34   | 0.31  | 4.35      |

In addition, the vibrations of $B$, $G$ and $E$ with pressure are shown in Figure 6. The values of bulk modulus $B$ and Young’s modulus $E$ increase with the increase in pressure, and the resistance to compression deformation and elastic deformation increase significantly with the increase in pressure. It can be seen from Figure 6 that the shear modulus $G$ of the Mg$_{23}$Al$_{30}$ mesophase increases slightly with the increase in pressure. The ability of the Mg$_{23}$Al$_{30}$ mesophase to resist plastic deformation becomes slightly stronger. It can be concluded that the resistance of Mg$_{23}$Al$_{30}$ to deformation can be improved by applying pressure.

For a trigonal system, the following formulas can calculate $B$, $G$, $E$ and $\nu$ (3), (4), (5), (6) [32]:

$$B = \frac{B_V + B_R}{2}$$  \hspace{1cm} (3)

$$G = \frac{G_V + G_R}{2}$$  \hspace{1cm} (4)

$$E = \frac{9BG}{3B + G}$$  \hspace{1cm} (5)

$$\nu = \frac{3B - 2G}{2(3B + G)}$$  \hspace{1cm} (6)

In addition, the empirical criterion put forward by Pugh, $G/B = 0.57$, is used as the critical value to predict the ductility and brittleness of the material [33]. If $G/B < 0.57$, it is a ductile material;
if $G/B > 0.57$, it is a brittle material. The calculated results of $G/B$ are shown in Table 4. After this calculation, the value is less than 0.57 for all pressure data; indicating that under these pressures, Mg$_{23}$Al$_{30}$ is a ductile material. As the pressure increases, the value of $G/B$ decreases. This shows that the ductility of the material is better with the increase in the pressure.

![Figure 6. Elastic modulus of Mg$_{23}$Al$_{30}$ under different pressures.](image)

We can also see the toughness and brittleness by Poisson’s ratio $v$ [34]. If $v < 1/3$, the material is brittle; if $v \approx 1/3$, the material is tough. According to the data in Table 3, Poisson’s ratio $v$ of the Mg$_{23}$Al$_{30}$ materials are all approximately equal to 1/3, indicating that Mg$_{23}$Al$_{30}$ is a ductile material, which is consistent with the conclusion obtained by the $G/B$ criterion.

The hardness $H_v$ can be used to measure the wear resistance of the material. The higher the hardness value, the better the wear resistance of the material [35]. Equation (7) can be used to calculate $H_v$ [36,37]:

$$H_v = \frac{(1 - 2v)E}{6(1 + v)}$$  \hspace{1cm} (7)

Figure 7 shows the hardness value of the Mg$_{23}$Al$_{30}$ mesophase under pressure. As can be seen from the diagram, with the increase in pressure, the wear resistance gets better. Compared with our previous study, the mechanical properties of Mg$_{17}$Al$_{12}$ are better than those of Mg$_{23}$Al$_{30}$ [6]. Meanwhile, the ductile properties of Mg$_{23}$Al$_{30}$ impede the strength of the Al matrix. After the first principle calculation, it can be easily suggested that this compound is the main reason for the low welding strength of magnesium/aluminum as dissimilar metals.

![Figure 7. Hardness value of the Mg$_{23}$Al$_{30}$ mesophase under pressure.](image)
4. Conclusions

The lattice constants of the Mg$_2$Al$_{30}$ equilibrium crystal structure indicates that the calculated results in this paper have a strong reliability. With the increase in pressure, the lattice constants $a$ and $c$ and volume $V_0$ of Mg$_2$Al$_{30}$ experience a decreasing trend. Meanwhile, the decreasing range of $c$ is greater than that of $a$, which indicates the material’s anisotropy. There is a strong resistance to volume change, plastic deformation and elastic deformation according to the calculation.

The energy band structure and state density of Mg$_2$Al$_{30}$ under pressure are obtained in the present manuscript. The charge density of Mg$_2$Al$_{30}$ can indicate that the structure of Mg$_2$Al$_{30}$ is characterized by metal bonds between adjacent Mg atoms, as well as ionic bonds between Mg atoms and Al atoms, and covalent characteristics between adjacent Al atoms.

The mechanical properties of Mg$_2$Al$_{30}$ can confirm that Mg$_2$Al$_{30}$ not only behaves as a stable crystal structure, but also has elastic stability. After judgment by Pugh’s empirical criterion, Mg$_2$Al$_{30}$ belongs to the ductile materials and displays anisotropy. In the range of 0–8 GPa, the volume modulus $B$, Young’s modulus $E$, shear modulus $G$ and the hardness of Mg$_2$Al$_{30}$ materials all increase with the increase in pressure and they show good elastic stability. The ductile properties of Mg$_2$Al$_{30}$ generally harm the strength of the Al matrix and it can be easily suggested that this compound is the main reason for the low welding strength of magnesium/aluminum as dissimilar metals.

Author Contributions: Conceptualization, methodology, Y.Z.; Writing—original draft preparation, L.S.; Writing—review and editing, W.Z., H.D.; Data curation, W.H.; Investigation, visualization, Y.L.; Software, J.P.; Investigation, Q.G., Y.L.; Visualization, M.D. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the State Key Laboratory for the Mechanical Behavior of Materials (20192110), the Open Fund of the National Joint Engineering Research Center for Abrasion Control and the Molding of Metal Materials (HKDNM201811) and the Natural Science Basic Research Plan in the Shaanxi Province of China (2019JQ-821).

Acknowledgments: The authors would like to express their gratitude to Yefei Li and Bing Xiao (Xi’an Jiaotong University) for their help in the DFT calculation and Zhiwei Liu (Xi’an Jiaotong University) for his help in the alloy fabrication.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Yang, Y.; Li, J.Q.; Song, H.B.; Liu, P.C. Research situation on addiction of magnesium alloys and its forming technology. Hot Work. Technol. 2013, 42, 24–27.
2. Polmear, I.J. Magnesium alloys and addiction. Mater. Sci. Technol. 1994, 10, 1–16. [CrossRef]
3. Li, X.K.; Zhang, Z.M.; Zhao, Y.L. Research and future development of wrought magnesium alloy. Hot Work. 2011, 40, 54–55.
4. Liu, Z.; Cheng, N.; Zheng, Q.; Wu, J.; Han, Q.; Huang, Z.; Xing, J.; Li, Y.; Gao, Y. Processing and tensile properties of A356 composites containg in situ small-sized Al$_3$Ti particulates. Mater. Sci. Eng. A 2018, 710, 392–399. [CrossRef]
5. Hort, N.; Huang, Y.; Kainer, K.U. Intermetallics in magnesium alloys. Adv. Eng. Mater. 2006, 8, 235. [CrossRef]
6. Zhou, Y.; Dang, M.; Sun, L.; Zhai, W.; Dong, H.; Gao, Q.; Zhao, F.; Peng, J. First-principle studies on the electronic structural, thermodynamics and elastic properties of Mg$_{17}$Al$_{12}$ intermediate phase under high pressure. Mater. Res. Express 2019, 6, 086501. [CrossRef]
7. Taub, A.I.; Luo, A.A. Advanced lightweight materials and manufacturing processes for automotive applications. Mrs Bull. 2015, 40, 1045. [CrossRef]
8. Mohammadi, J.; Behnamian, Y.; Mostafaei, A.; Izadi, H.; Saeid, T.; Kokabi, A.H.; Gerlich, A.P. Friction stir welding joint of dissimilar materials between AZ31B magnesium and 6061 aluminum alloys: Microstructure studies and mechanical characterizations. Mater. Charact. 2015, 101, 189–207. [CrossRef]
9. Wang, D.; Liu, J.; Xiao, B.; Ma, Z. Mg/Al reaction and Mechanical properties of AL alloy/Mg alloy friction stir welding Joints. Acta Metall. Sin. 2010, 46, 589. (In Chinese) [CrossRef]
10. Ben, A.A.; Munzti, A.; Kohn, G. The Minerals, Metals & Materials Society. In Proceedings of the TMS Annual Meeting, Seattle, WA, USA, 17–21 February 2002; p. 295.

11. Liu, Z.J.; Gong, Y.; Su, Y.M. Study on Characteristics in TIG Welded Joint of Mg/Al Dissimilar Materials. J. Mater. Eng. 2015, 43, 18. (In Chinese)

12. Azizi, A.; Alimardan, H. Transactions of Nonferrous Metals Society of China; Elsevier: Amsterdam, The Netherlands, 2016; p. 85.

13. Zhuang, H.; Chen, M.; Carter, E.A. Elastic and thermodynamic properties of complex Mg-Al intermetallic compounds via orbital-free density functional theory. Phys. Rev. Appl. 2017, 5. [CrossRef]

14. Huang, Z.W.; Zhao, Y.H.; Hou, H.; Han, P.D. Electronic structural, elastic properties and thermodynamics of Mg17Al12, Mg2Si and Al2Y phases from first-principles calculations. Phys. B 2012, 407, 1075–1081. [CrossRef]

15. Hu, W.C.; Liu, Y.; Hu, X.W.; Li, D.J.; Zeng, X.Q.; Yang, X.; Xu, Y.X.; Zeng, X.S.; Wang, K.G.; Huang, B.L. Predictions of mechanical and thermodynamic properties of Mg17Al12 and Mg2Sn from first-principles calculations. Philos. Mag. 2015, 95, 1626–1645. [CrossRef]

16. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169. [CrossRef] [PubMed]

17. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50. [CrossRef]

18. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 1999, 59, 1758. [CrossRef]

19. Blöchl, P.E. Projector augmented-wave method. Phys. Rev. B 1994, 50, 17953. [CrossRef]

20. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865. [CrossRef]

21. Samson, S.; Grodon, E.K. The Crystal Structure of ε-Mg23Al30*. Acta Cryst. Hica Sect. B 1968, 24, 1004. [CrossRef]

22. Wang, Z.L.; Wei, Z.J.; Wang, H.W.; Cao, L. Effects of high pressure on microstructure and phase of Al-Mg-Zn alloy. Int. J. Cast Met. Res. 2006, 19, 269–273. [CrossRef]

23. Hu, J.Q.; Xie, M.; Chen, J.L.; Liu, M.M.; Chen, Y.T.; Wang, S.B.; Li, A.K. First principles study of electronic and elastic properties of Ti3AC2 (A = Si, Sn, Al, Ge) phases. Acta Phys. Sin. 2017, 66, 270–279.

24. Chen, L.; Peng, P.; Li, G.; Liu, J.; Han, S. First-principle calculation of point defective structures of B2-RuAl intermetallic compound. Rare Met. Mater. Eng. 2006, 35, 1065. (In Chinese)

25. Sahu, B.R. Electronic structure and bonding of ultralight LiMg. Mater. Sci. Eng. B 1997, 49, 74–78. [CrossRef]

26. Fan, K.M.; Yang, L.; Tang, J.; Sun, Q.G.; Zu, X.T. First-Principles Study of the Elastic Properties of Hexagonal Phase ScA6 (A = H, He). In Advanced Materials Research; Trans Tech Publications Ltd.: Stafa-Zurich, Switzerland, 2013; Volume 690.

27. Parlinski, K.; Li, Z.Q.; Kawazoe, Y. First-principles determination of the soft mode in cubic ZnO2. Phys. Rev. Lett. 1997, 78, 4064–4066. [CrossRef]

28. Vanderbilt, D. Density-functional study of bulk and surface properties of titanium nitride using different exchange-correlation-functionals. Phys. Rev. B 2000, 62, 2899.

29. Sinko, G.V.; Smirov, N.A. Ab initio calculations of elastic constants and thermodynamic properties of bcc, fcc, and hcp Al crystals under pressure. Phys. Condens. Matter. 2002, 14, 6989.

30. Liu, Y.; Hu, W.C.; Li, D.J.; Zeng, X.Q.; Xu, C.S.; Yang, X.J. First-principles investigation of structural and electronic properties of MgCu2 Laves phase under pressure. Intermetallics 2012, 31, 257–263. [CrossRef]

31. Li, Y.F.; Xiao, B.; Sun, L.; Gao, Y.M.; Cheng, Y.H. Phonon optics, thermal expansion tensor, thermodynamic and chemical bonding properties of Al4SiC4 and Al4Si2C3: A first-principles study. RSC Adv. 2016, 6, 43191. [CrossRef]

32. Matteisini, M.; Ahuja, R.; Johansson, B. Cubic Hf3N4 and Zr3N4: A class of hard materials. Phys. Rev. B 2003, 68, 184108.

33. Wu, Z.J.; Zhao, E.J.; Xiang, H.P.; Hao, X.F.; Liu, X.J.; Meng, J. Crystal structures and elastic properties of superhard IrN2 and IrN3 from first principles. Phys. Rev. B 2007, 76, 054115. [CrossRef]

34. Pugh, S.F. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. Lond. Edinb. Dublin Philos. Mag. J. Sci. 1954, 45, 823–843. [CrossRef]

35. Frantsevich, I.N.; Voronov, F.B.; Bokuta, S.A. Elastic Constants and Elastic Moduli of Metals and Insulators Handbook; Naukovia Dumka Publishing House: Kiev, Ukraine, 1983; pp. 60–180.
36. Richard, R.C.D. The wear of metals by hard abrasives. *Wear* 1967, 10, 291–309. [CrossRef]

37. Wang, J.; Hou, H.; Zhao, Y.H.; Han, P.D. First-principles study of mechanical properties and electronic structures of the nickel-molybdenum binary compounds under pressure. *Rare Met. Matter Eng.* 2018, 47, 846–852.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).