Electronic and Elastic Properties of CaMg$_2$ Alloy Phase under Various Pressures by Density Functional Theory

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Abstract. The influencing effect of pressure on structural, elastic and electronic properties of CaMg$_2$ Laves phase is mainly investigated. The optimized structural parameters at zero pressure are $a=b=6.250\,\text{Å}$, $c=10.101\,\text{Å}$, which has good agreement with the experimental and theoretical values. The elastic constants are calculated, and then the bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio and anisotropy factor are determined. The results show that the applied pressure is beneficial to the elastic properties of CaMg$_2$. The analysis of electronic density of states (DOS) and Mulliken electron population reveal the bonding characteristics in CaMg$_2$ crystal. Finally, the Debye temperatures under different pressures are obtained from the average sound velocity.

1 Introduction

Magnesium alloys as low density, high specific strength, good stiffness and strength-weight ratio are widely used in aerospace industry, automobile industry, 3D printing and other fields[1,2]. Magnesium alloys can be significantly improved by adding rare-earth (RE) elements[3] and Ca element[4]. Mg-Ca alloy exhibits excellent oxidation-resistance and burning-resistance[5], and it is also regarded as one of the most promising alloy due to its appreciable corrosion resistance[6]. CaMg$_2$ Laves phase as its excellent physical and chemical properties is a typical phase in Mg-Y-Ni[7] and Mg-Al-Ca alloy[8]. Yu et al. [9] investigated the electronic structure and elastic properties of the binary AB2 type Laves phase in Mg-Al-Ca alloys. Elastic constants of CaMg$_2$ alloy are studied by Tang et al.[2]. Zhou et al. [6] has investigated the phase stability and electronic structure of an Mg-Ca system, showing that CaMg$_2$ Laves phase is ductile with a structural stability. However, there is no report about the experimental values of Debye temperature and the effect of pressure on structural, elastic and electronic properties of CaMg$_2$ Laves phase. In this work, the first-principles calculations are used to investigate the anisotropic elasticity and electronic properties of the CaMg$_2$ Laves phase under pressure. Moreover, the density of state (DOS) under different pressure is analyzed to insight into the bonding characteristics of CaMg$_2$, and then reveals the underlying structural stability mechanism of CaMg$_2$ Laves phase. The current work can act as a theoretical prediction and provides mechanical parameters of CaMg$_2$ alloy.

2 Theoretical principle and calculation algorithm

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2.1 Description of elastic constants algorithm and Young’s modulus calculation

A multi-particle electronic structure satisfies the Schrödinger equation. Generally, Hamiltonian contains kinetic energy, Coulomb potential energy between electrons and the external potential, which is described as:

\[ H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i,j} \frac{e^2}{|r_i - r_j|} + \sum_i V_i(r) \]  

(1)

Where, \( V_i(r) \) is an external potential; \( r_i \) and \( r_j \) are the nucleus position vectors; while \( m \) and \( e \) stand respectively for the mass of nuclei and electrons. \( \hbar \) is the reduced Planck constant.

Kohn-Sham equation as an approximation to simplify Schrödinger equation is described as[10]:

\[
\begin{align*}
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r)\right] \varphi_i(r) &= \varepsilon_i \varphi_i(r) \\
V_{eff}(r) &= V(r) + V_{xc}(r) + V_{es}(r) \\
\rho(r) &= \sum_i |\varphi_i(r)|^2 \\
\end{align*}
\]

(2)

Where, \( \rho(r) \) is the electron density. Equation (2) includes not only the nucleus and electron kinetic energy term but also term of nucleus- nucleus and electron-electron interactions[10]. The electron density is optimised and elastic constants are obtained.

For hexagonal structure, mechanical stability condition and Voigt/Reuss bounds of elasticity can be obtained by means of Voigt and Reuss bounds, which are based on the Hill average and Young’s modulus can be determined.

Based on C_{ij}, Debye temperatures can be estimated by the some sound velocity equations[12]:

\[
\Theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi M} \left( \frac{N_a \rho}{M} \right)^{1/3} \right]^{1/2} V_m, \quad V_m = \left[ \frac{1}{3} \left( \frac{2}{V_s^3} + \frac{1}{V_l^3} \right) \right]^{1/3}, \quad V_s = \sqrt{\frac{G}{\rho}}, \quad V_l = \sqrt{\frac{B + \frac{4}{3}G}{\rho}}
\]

(6)

Where \( \Theta_D \) is Debye temperature; \( h \) and \( k_B \) are the Planck and Boltzmann constant; \( n \) is the total number of atoms; \( \rho \) is density; \( N_a \) the Avogadro number; \( M \) the molecular weight per formula; \( V_m \) the average sound velocity; \( V_s \) the transverse sound velocity and \( V_l \) the longitudinal sound velocity.

2.2 Description of CaMg2 modeling and computational method

Fig.1 shows CaMg2 crystal of hexagonal structure with a space group P63/mmc. Ca atoms are located on 4f sites and Mg atoms 2a, 6f sites. Pseudo atomic calculations are performed for Mg 2p6 3s2 and Ca 3s2 3p6 4s2.

Crystal lattice (a=b=6.250Å, c=10.101Å, α=β=90°, γ=120°) is shown in Fig.1 a). DFT calculation is shown in Fig.1 b), initial conditions are as: the exchange-correlation function is generalized gradient approximation (GGA); Cutoff energy of the plane waves for ultrasoft pseudopotentials is 400 eV.
Brillouin zone is $12 \times 12 \times 8$ by Monkhorst-Pack method. The self-consistent convergence of the total energy is $5.0 \times 10^{-6} \text{eV per atom}$ and convergence of the force on all atoms is less than $0.001 \text{eV/nm}$, the pressure region is $0 \sim 60 \text{GPa}$.

Figure. 1  a) Final parameters of CaMg$_2$ crystal; b) Flowchart of DFT by solving Kohn-Sham equations

3 Results and discussion

3.1 Structural parameters and elastic constants

The equilibrium lattice parameters, elastic constants $C_{ij}$ and bulk modulus $B_0$ are in Tab.1.

Table.1 The structural parameters ($a_0$, $c_0$, $c_0/a_0$, $V_0$), elastic constants and bulk modulus $B_0$ of CaMg$_2$ phase at 0GPa.

<table>
<thead>
<tr>
<th>a) Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ ($\text{Å}$)</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>This work</td>
</tr>
<tr>
<td>Cal.[10]</td>
</tr>
<tr>
<td>Exp.[7]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) Elastic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>This work</td>
</tr>
<tr>
<td>Cal.[9]</td>
</tr>
<tr>
<td>Cal.[3]</td>
</tr>
</tbody>
</table>

As the values in Tab.1 match well with experimental values, it is indicated that the present model is reliable. Variations of lattice parameter and elastic constants with increase of pressure are in Fig.2.
As shown in Fig. 2 a), it can be seen that CaMg$_2$ has not undergone a phase transition according to the smooth variation of $a/a_0$, $c/c_0$ and $V/V_0$ with the increase of pressure. Moreover, it shows that the lattice parameter $a$ and parameter $c$ are almost equal throughout the whole pressure range, indicating that the elastic anisotropy of CaMg$_2$ is weak. The compressive ability of CaMg$_2$ crystal under pressure is consistent with the variation trend of the $V/V_0$ curve. The axial ratio $c/a$ changes little with increase of pressure, from minimum 1.615 to maximum 1.618. As in Fig. 2 b), we can conclude that $C_{11}$ and $C_{33}$ are more sensitive to the change of applied pressure than $C_{12}$ and $C_{13}$. Besides, the applied pressure has less effect on $C_{44}$ and $G$, while $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, bulk and Young’s modulus show the increasing tendency with the increase of pressures.

### 3.2 Prediction of elastic moduli of CaMg$_2$ polycrystals

To investigate the effect of the applied pressure on structural properties of CaMg$_2$, the changes of Poisson’s ratio and $G/B$ with increasing pressure are plotted in Fig. 3.

**Figure.3** The pressure independence of Poisson’s ratio and the $G/B$ ratio of CaMg$_2$

As shown in Fig. 3, the $G/B$ ratio decreases with the increasing pressure. Poisson’s ratio at 0GPa is 0.27, showing CaMg$_2$ is with predominantly central interatomic forces. The critical value which separates brittleness and ductility is about 0.57 in the horizontal dotted line. Evidently, the $G/B$ ratio within region of 0~4GPa is higher than critical value 0.57 at 4GPa, which implies that CaMg$_2$ phase show a little brittle at 0GPa ($G/B = 0.63$) and turn to be a ductile behavior after critical value. It is
indicated that CaMg$_2$ shows slight brittleness under 0~4GPa and good ductility under 4~60GPa.

### 3.3 Analysis of the density of state (DOS) and bonding characteristics

Fig. 4 shows the total and partial DOS of CaMg$_2$ phase near Fermi level under 0GPa in Fig. 4 a), 20GPa in Fig. 4 b), 40GPa in Fig. 4 c) and 60GPa in Fig. 4 d).

As in Fig.4, the total DOS of CaMg$_2$ is mainly made up of the $s$, $p$ states of Mg atoms below Fermi level and the $s$, $p$ states of Ca atoms above Fermi level. It is evident that the total DOS of CaMg$_2$ decreases with elevated pressure, which implies that applied pressure is of benefit to the stability of CaMg$_2$. Moreover, CaMg$_2$ is characterised to have the metallic behaviour as there is no energy gap near the Fermi level[2,6,8,9]. The main bonding peak is located in the energy region from -2 to 4eV, originated from the contribution of valence electron numbers of Mg $s$, Mg $p$, Ca $s$ and Ca $p$ orbits. A hybridization of Mg $s$, $p$ and Ca $s$, $p$ orbits is seen in Fig.4 a), indicating the existence of covalent bonding in CaMg$_2$ crystal. From Fig.4 b) to Fig.4 d), the shifting of Mg $s$ and $p$ orbits from higher to lower energy region is discovered. Moreover, with increasing pressure, the Ca $s$ and $p$ orbits present a slight broadening and a decrease of intensity, which indicates that the hybridization of Mg $s$, $p$ and Ca $s$, $p$ orbits is becoming stronger. It is worthwhile to note that the applied pressure has a little effect on the DOS when the pressure is above 40GPa.

![Figure 4](image)

**Figure.4** The total and partial density of states (DOS) of CaMg$_2$: a) at 0GPa; b) at 20 GPa; c) at 40 GPa; d) at 60 GPa.

### 3.4 Analysis of Mulliken electron population and Debye temperature

The Mulliken electron population has been performed to consider the ionic bond feature of CaMg$_2$ phase. Table 4 shows the Mulliken electron population of CaMg$_2$ under pressure.
Table 2: a) Mulliken electron population of pressure; b) Pressure dependence of parameter $\rho$, $V_s$, $V_l$, $V_m$ and $\Theta_D$

<table>
<thead>
<tr>
<th>Pressure(GPa)</th>
<th>Species</th>
<th>$s$</th>
<th>$p$</th>
<th>$d$</th>
<th>Total</th>
<th>Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Ca</td>
<td>2.44</td>
<td>6.00</td>
<td>0.66</td>
<td>9.10</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>Mg (I)</td>
<td>0.92</td>
<td>7.45</td>
<td>0.00</td>
<td>8.37</td>
<td>-0.37</td>
</tr>
<tr>
<td></td>
<td>Mg (II)</td>
<td>0.93</td>
<td>7.55</td>
<td>0.00</td>
<td>8.48</td>
<td>-0.48</td>
</tr>
<tr>
<td>30</td>
<td>Ca</td>
<td>2.32</td>
<td>5.98</td>
<td>1.00</td>
<td>9.30</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>Mg (I)</td>
<td>0.89</td>
<td>7.31</td>
<td>0.00</td>
<td>8.20</td>
<td>-0.20</td>
</tr>
<tr>
<td></td>
<td>Mg (II)</td>
<td>0.90</td>
<td>7.50</td>
<td>0.00</td>
<td>8.40</td>
<td>-0.40</td>
</tr>
<tr>
<td>60</td>
<td>Ca</td>
<td>2.27</td>
<td>5.96</td>
<td>1.25</td>
<td>9.48</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Mg (I)</td>
<td>0.93</td>
<td>7.09</td>
<td>0.00</td>
<td>8.02</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>Mg (II)</td>
<td>0.95</td>
<td>7.39</td>
<td>0.00</td>
<td>8.34</td>
<td>-0.34</td>
</tr>
</tbody>
</table>

(Note: $\rho$ is density, $V_s$ transverse sound velocity, $V_l$ longitudinal sound velocity, $V_m$ average sound velocity, $\Theta_D$ Debye temperature.)

As in Tab.2 a), the total charge transfer from Ca atoms to Mg atoms at $0GPa$ is 3.60, at $30GPa$ is 2.80 and at $60GPa$ is 2.08. The charge transfer from Ca atoms to Mg atoms demonstrates the ionic bonding in CaMg$_2$ crystal. It is found that the charge transfer from Ca to Mg decreases with the increasing pressure, implying that the ionic bonding is getting weaker\[8\] under the higher pressure.

Tab.2 b) has listed the calculated $V_s$, $V_l$, $V_m$ and $\Theta_D$ from 0 $\sim$ 60 GPa of CaMg$_2$. Debye temperature at 0 GPa is 348.70 K, and it is clear that the Debye temperature increases under 0 $\sim$ 30GPa with increasingly applied pressure then presents a declining trend when the applied pressure is above 30GPa.

4 Conclusions

Structural, elastic and electronic properties of CaMg$_2$ Laves phase under external pressure from 0 $\sim$ 60GPa are investigated by DFT. Conclusions are as follows:

1) The optimized structural parameters ($a=b=6.250\text{Å}$, $c=10.101\text{Å}$, $V=341.732\text{ Å}^3$) are very close to experimental values. From DFT calculation, CaMg$_2$ Laves phase under 0 $\sim$ 60GPa does not undergo a phase transition, and the compressibility in $a$ direction is better than in $c$ direction.

2) Based on elastic constants by DFT, the mechanical parameters of CaMg$_2$ are as: bulk modulus 29.659 GPa, shear modulus 18.553 GPa, Young’s modulus 49.286 GPa, Poisson’s ratio 0.196 and elastic anisotropy factor $A$. The $G/B$ ratio shows a decreasing tendency with the increase of pressure.

3) From DOS analysis at 0, 20, 40 and 60GPa show that below Fermi level the total DOS is mainly Mg $s$, $p$ orbits while above Fermi level the total DOS is almost Ca $s$, $p$ orbits. Moreover, covalent bonding is existed in CaMg2 crystal according to the orbital hybridization of Mg $s$, $p$ and Ca $s$, $p$ orbits. Mulliken electronic population demonstrate the charge transfer from Ca to Mg becomes less thus the ionic bond between Ca and Mg becomes weaker with the increase of pressure.

4) The Debye temperature shows an increasing tendency with the applied pressure from 0 $\sim$ 30
GPa and then presents a declining tendency under the pressure region of 30 GPa～60GPa.

References