Structural and elastic properties of CaMg2 Laves phase by Y-parameter and Reuss-Voigt-Hill methods

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Abstract. Structural, mechanical properties of CaMg2 Laves phase are investigated by the first-principle calculations and then the homogenized moduli are calculated by both the classical Reuss-Voigt-Hill estimation and a so-called Y parameter. Above all, the optimized crystal parameters are in very good agreement with the experimental data reported. Besides, elastic constants Cij are calculated, thus the shear modulus, bulk modulus, Young’s modulus, Poisson’s ratio are calculated to compare with the relative data in references. Contrary to Hill approach, the Y parameter enables to investigate the anisotropic characteristics and isotropic elastic properties of CaMg2 structure. By using Y parameter, we can see that Young’s modulus and Poisson’s ratio as a function of the compliance coefficient Sij (or elastic constants Cij) and plane orientation are distributed within a reasonable range, which are useful for the DFT study of similar hexagonal crystal structure at nanoscale.

1. Introduction
Magnesium (Mg) alloys cause more attention in recent years, as the best strength to weight ratio, low density and good stiffness [1, 2]. However, the practical application of magnesium alloys has not been widely used due to their restricted mechanical properties, as it easy to be oxidized as well as the limited mechanical properties [3, 4]. Besides, by adding rare-earth (RE) elements, the mechanical properties of Mg-alloys can be greatly improved [5]. Besides, Ca can normally raise the density of aging precipitates MgZn2 phase, therefore can improve the mechanical properties of the Mg-alloy [6]. Mg–Ca alloy has the combustion resistance and good oxidation [7]. The binary system of Mg–Ca has a good biocompatibility, no toxicity and appreciable corrosion resistance [8]. Zhang et al. [9] investigated the structural and thermodynamic properties of CaMg2 in Mg–Al–Ca system. Ortega et al. [10] investigated the precipitation process of CaMg2 in Mg–Ca–(Zn) alloys by using positron annihilation spectroscopy. Zhong et al. [11] investigated the thermodynamic data of C14, C15 and C36 structures of CaMg2. Moreover, as its excellent physical and chemical properties [12, 13] in Mg–Ca, Mg–Al–Ca and Mg–Zn–Ca alloy systems, CaMg2 Laves phase has caused more attention. Experimentally, some Laves phases CaAL2 (C15), CaMg2 (C14), (Mg,Ca)Al2 (C14) and Ca(Mg,Al)2 (C36) in Mg–Al–Ca alloys have been investigated [14, 15]. Theoretically, Yu et al. [16] studied the mechanical properties of the AB2-
type Laves, discovering that the CaMg$_2$ phase has a strong structural stability and the alloying ability. Tang et al. [3] investigated the elastic properties of CaMg$_2$ Laves phase, which suggests that CaMg$_2$ Laves phase has a strong stability. The stability and mechanical properties of the Mg-Ca system was studied by Zhou et al. [8], with the conclusion that CaMg$_2$ phase is ductile. Mao et al. [18] investigated the mechanical properties of intermetallics in the Mg-Zn-Ca-Cu alloy. However, there is no theoretical systematically study reported about the structural, mechanical properties of CaMg$_2$ phase. Elastic moduli of polycrystals can be calculated by Y-parameter and the Reuss-Voigt-Hill (RVH) methods [20- 24]. Musgrave [25] and Neighbours [26] have discussed the propagation velocities of sound for different crystal symmetries.

In this work, the Y-parameter and Reuss-Voigt-Hill (RVH) methods are used to investigate elastic properties of the CaMg$_2$ phase. Hence, this work aim to study about the elastic properties of C14-type CaMg$_2$ phase on the basis that Young’s modulus is the function of the elastic constants in a certain orientation of the crystal plane. These are useful for similar hexagonal structure with the same space group P63/mmc at nanoscale.

2. Modelling and computational method

2.1 Modelling of CaMg$_2$ crystal

Manganese carbonate crystals belong to the hexagonal type, the space group is P63/mmc type, and the lattice parameters are as follows: $a=b=6.25\text{Å}$, $c=10.10\text{Å}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. Its crystal structure is in Figure 1.

![Figure 1. Schematic diagram of CaMg$_2$ crystal structure.](image)

As in Figure 1, Mg atoms are located on $2a$, $6f$ sites. Besides, Ca atoms are located on $4f$ sites. For Mg $2p6 \ 3s2$ and Ca $3s2 \ 3p6 \ 4s2$, the Pseudo atomic calculations are carried out. The lattice parameters are optimized for energy minimization.

2.2 computational method

CASTEP as an first-principles plane wave pseudo-potential method is used for the calculations. The exchange correlation potential is considered by the generalized gradient approximation (GGA). The cut-off energy of the plane wave is set as 400eV to fully converge during calculation. The Brillouin zone with a mesh of $12\times12\times8$ is generated by Monkhorst-Pack method. Geometry optimization is carried out with optimizing cell by the scheme of the Brodyden - Fletcher - Goldfarb - Shanno (BFGS) minimization until the total energy convergence value is $5.0\times10^{-6}$ eV/atom, the pressure region is $0\sim 60\text{GPa}$.

3 Result analysis and discussion
3.1 Lattice parameters and elastic constants

3.1.1 Lattice parameters

The lattice parameters at 0MPa are shown in Table 1.

|            | \(a_0(\text{Å})\) | \(c_0(\text{Å})\) | \(c_0/a_0\) | \(V_0(\text{Å}^3)\) |
|------------|-------------------|-------------------|-------------|-------------------|
| This work  | 6.250             | 10.101            | 1.616       | 341.732           |
| Cal. [3]   | 6.232             | 10.093            | 1.620       | 339.740           |
| Exp. [16]  | 6.220             | 10.100            | 1.624       | 341.081           |
| Cal. [17]  | 6.240             | 10.140            | 1.625       | 342.200           |

From Table 1, the c/a ratio used is 1.616, within the relative error range of the experiment, which match better to Tang [3] 1.620, Aono [16] 1.624 and Yu [17] 1.625.

3.1.2 Elastic constants

Elastic constants \(C_{ij}\) (GPa) of CaMg₂ crystal is in Table 2.

| \(C_{11}\) | \(C_{12}\) | \(C_{13}\) | \(C_{33}\) | \(C_{44}\) |
|----------|----------|----------|----------|----------|
| This work| 55.70    | 18.05    | 15.26    | 58.39    | 16.95    |
| Cal. [5] | 62.95    | 15.27    | 13.64    | 65.20    | 17.77    |
| Cal. [18]| 51.43    | 22.31    | 14.73    | 58.51    | 14.32    |
| Exp. [27]| 56.25    | 15.90    | 15.00    | 61.63    | 18.05    |

From Table 2, we can see that \(C_{33}\) is the largest, indicating that the stiffness in this direction is the largest. \(C_{33}\) in c-axis direction is perpendicular to the atomic plane composed of \(a\)-axis and \(b\)-axis. Elastic constants \(C_{ij}\) under various pressures of 0-60GPa is in Figure 2.

![Figure 2. Elastic constants under pressure of 0-60GPa](image)

Figure 2. Elastic constants under pressure of 0-60GPa

From Figure 2, the variation of elastic constants under different pressures is not the same, where the slope of the \(C_{11}\) and \(C_{33}\) change curves is positive. The contribution of \(C_{33}\) to elasticity is greater
than that of the $a$-axis $C_{11}$ and the $b$-axis $C_{22}$. The rest elastic constants slightly increased but tended to be relatively steady.

3.2 Reuss bound and Voigt bound

3.2.1 Reuss bound and Voigt bound

For hexagonal crystals [21], the elastic constants should satisfy the generalized stability criteria. Generally, the Reuss and Voigt bounds of hexagonal crystals are as [21]:

\[
C_{11} > 0; C_{11} - C_{12} > 0; C_{44} > 0; (C_{11} + C_{12})C_{13} - 2C_{44}^2 > 0
\]  

\[
G_r = \frac{1}{30} (7C_{11} - 5C_{12} + 12C_{44} + 2C_{13} - 4C_{13}^2)
\]  

\[
G_x = \frac{5}{2} \left\{ \frac{[(C_{11} + C_{12})C_{13} - 2C_{44}^2][C_{44}C_{66}]}{2C_{44}C_{66} + [(C_{11} + C_{12})C_{13} - 2C_{44}^2][C_{44} + C_{66}]} \right\}
\]  

\[
B_r = \frac{2}{9} \left(C_{11} + C_{12} + \frac{1}{2}C_{33} + 2C_{13}\right)
\]  

\[
B_x = \frac{(C_{11} + C_{12})C_{33} - 2C_{44}^2}{C_{11} + C_{12} + 2C_{13} - 4C_{13}^2}
\]

Based on the upper boundary (Voigt bound) and lower boundary (Reuss bound), elastic moduli can be calculated [21,23] as follows: $G_r=18.63\text{GPa}$, $B_r=29.66\text{GPa}$, $G_x=18.48\text{GPa}$, $B_x=29.65\text{GPa}$, $B=25.66\text{GPa}$, $G=18.55\text{GPa}$, $E=46.05\text{GPa}$, $\mu=0.241$. Besides, values of the B (29.66GPa) and G (18.55GPa) are consistent with the values of 29.43GPa and 15.72GPa by the experimental measurement of Mao [18].

3.2.2 The compliance coefficient

Elastic constant characterizes the response of the lattice to external stress within the elastic limit [8]. For hexagonal crystal, the interchangeable relation between $C_{ij}$ and $S_{ij}$ are as follows [28]:

\[
S_{11} = \frac{C_{11}}{2C_{13}(C_{11} + C_{12}) - 2C_{11}^2} + \frac{1}{2(C_{11} - C_{12})}
\]  

\[
S_{12} = \frac{C_{12}}{2C_{13}(C_{11} + C_{12}) - 2C_{12}^2} + \frac{1}{2(C_{11} - C_{12})}
\]  

\[
S_{13} = -\frac{C_{13}}{C_{13}(C_{11} + C_{12}) - 2C_{13}^2}
\]  

\[
S_{33} = \frac{C_{11} + C_{12}}{C_{13}(C_{11} + C_{12}) - 2C_{13}^2}
\]  

\[
S_{44} = \frac{1}{C_{44}}
\]

Young's modulus describes the linear deformation behaviors of the crystal, its value in three directions of $a$, $b$, and $c$ axes can be obtained from the inverse $S_{ij}$ matrix in Cartesian coordinates: $E_x = S_{11}^{-1}$, $E_y = S_{22}^{-1}$, And $E_z = S_{33}^{-1}$. The $S_{ij}$ can be obtained by inverse matrix.

Thus, the compliance coefficient $S_{ij}$ can be calculated as: $S_{11}=0.0209$, $S_{33}=0.0590$, $S_{12}=-0.0057$, $S_{13}=-0.0040$. By the definition, thus: $E_x=E_y=47.8469\text{GPa}$, $E_z=16.9492\text{GPa}$.

3.2.3 $Y$-parameter expressions

Based on the Reuss bound, $Y$ parameter including elastic modulus $E_Y$ and Shear modulus $G_Y$ of the hexagonal crystal surface normal $(n=(u, v, w))$ are as [29]:

\[
E_Y(u, v, w) = \frac{1}{2\left|S_{11} - \left[2(S_{11} - S_{13}) - S_{44}\right]w^2 + (S_{11} - 2S_{13} - S_{44})w^3\right|}
\]  

(11)
Where \( w \) is a normal direction cosine of hexagonal crystal surface.

Similarly, for Voigt bound, \( E_{Y} \) and \( G_{Y} \) are as [29]:

\[
E_{Y} = \frac{1}{4} \left[ 2C_{11} - C_{12} - C_{13} - w^{2}(5C_{11} - C_{12} - 5C_{13} + C_{33}) \right]
\]

(14)

When \( w^{2} = 1/3 \), Young's modulus is equal to the calculation result by Hill model.

Relations between compliance coefficient \( S_{ij} \) and Young's modulus \( \Phi \) (or shear modulus \( \Phi \)) in either direction of hexagonal crystal making an angle \( \Phi \) with \( c \)-axis are [28]:

\[
S_{ij} = \frac{1}{3} \left[ (1 - L_{3}^{2})^{2} \left( S_{ij} + (2S_{11} + S_{13})L_{3}^{2} \right) \right] \]

(15)

\[
\frac{1}{G_{ij}} = \frac{1}{2} \left[ (1 - L_{3}^{2})^{2} \left( S_{ij} - S_{11} - \frac{1}{2}(1 - L_{3}^{2}) \right) + 2(S_{11} + S_{13} - 2S_{12})L_{3}^{2} \right] \]

(16)

Where, \( L_{3} = \cos \theta \) is the cosine of normal orientation \( L_{3} \) within crystal plane of hexagonal crystal.

### 3.3 Elastic moduli by various methods

#### 3.3.1 Homogenized elastic moduli by RVH

Based on calculated \( C_{ij} \), homogenized moduli are obtained by RVH method. Voigt and Reuss approximations showing upper limit and lower limit are in Table 3, the difference within acceptable errors arises due to the use of different parameter \( C_{ij} \) in calculation.

| Table 3. Mechanical moduli (unit: GPa) of CaMg2 crystalline by various methods |
|-----------------|----------------|----------------|----------------|----------------|----------------|
| Bv  | Br  | Gv  | Gr  | B  | G  |
| This work | 29.66 | 29.65 | 18.63 | 18.48 | 29.66 | 18.55 |
| Cal. [5] | 30.69 | 30.69 | 21.78 | 21.24 | 30.69 | 21.51 |
| Cal. [18] | 29.43 | 29.43 | 15.95 | 15.50 | 29.43 | 15.72 |
| Exp. [27] | 29.55 | 29.51 | 19.80 | 19.66 | 29.53 | 19.73 |

From Table 3, we can see that elastic moduli by \( Y \)-parameter are consistent with the classical Reuss-Voigt-Hill (RVH) calculation. The relation \( G = E/[2(1+\nu)] \) are satisfied with parameters in Table 3 and Table 4.

#### 3.3.2 Surface of elastic modulus

The universal anisotropic index \( (A_{U}) \), the percentage of anisotropy in compression and shear \( (A_{B} \) and \( A_{C} \)) are [30]:

\[
A_{U} = 5G_{br} + B_{Br} - S, \quad A_{B} = \frac{G_{br} - G_{Br}}{G_{Br} + G_{br}} \times 100\%
\]

(17)

Where the \( B_{Vr}, \) \( B_{Br}, \) \( G_{V} \) and \( G_{0} \) refers to the Voigt and Reuss approximations of bulk modulus and shear modulus. \( A_{U} = 0 \) corresponds to isotropic structure. \( A_{C} = 1 \) stands for the largest elastic anisotropy.

Young’s modulus \( E \), Poisson’s ratio \( \nu \), bulk to shear modulus ratio \( B/G \), and elastic anisotropy indexes \( (A_{U} \) and \( A_{C} \)) are listed in Table 5.
Table 4. Young’s modulus E, Poisson’s ratio ν, bulk to shear modulus ratio B/G, and elastic anisotropy indexes (A_U and A_G).

| ν      | A_U | A_G | B/G | E (GPa) |
|--------|-----|-----|-----|---------|
| This work | 0.241 | 0.040 | 0.004 | 1.598 | 46.055 |
| Cal. [5]  | 0.216 | 0.127 | 0.013 | 1.427 | 52.309 |
| Cal. [18] | 0.273 | 0.143 | 0.014 | 1.872 | 40.043 |
| Exp.[27]  | 0.227 | 0.037 | 0.004 | 1.497 | 48.415 |

Surface of elastic modulus by DFT calculation of CaMg_2 compound is shown in Fig.4.

Figure 3. Surface of elastic modulus by DFT calculation of CaMg_2 crystal

From Figure 3, Young’s modulus and shear modulus are anisotropic, showing a certain anisotropy. Young’s modulus E of CaMg_2 compound is 46.055 GPa, which demonstrates manganese carbonate is a relatively stiffer material. Poisson ratio is 0.241, which is close to other references [5, 18, 27].

3.3.3 Elastic moduli variation by Y-parameter

Young’s and Poisson ratio of CaMg_2 structure by Y-parameter are in Figure 4.
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.

(b) Shear modulus

Figure 4. Young’s modulus and Poisson ratio of CaMg$_2$ by the Y parameter

As from Fig.4 a) - Fig.4 b), Young’s modulus and Poisson's ratio of CaMg$_2$ are closed to each other. Moreover, Young’s modulus $E$ is between 43.77GPa and 52.07GPa, Poisson ratio $\nu$ is between 0.207 and 0.254. Elastic moduli of CaMg$_2$ compound based on $C_{ij}$ can be calculated by RVH estimation\[^{21-24}\]. It can be seen that, when $w^2=1/3$, values of $E$ and $\nu$ are 46.05GPa and 0.24, which are equal to results of Hill model.

4. Conclusion

Generally, elastic properties of CaMg$_2$ crystal is investigated and $C_{ij}$ determination are given by DFT method. Y-parameters have then been determined for CaMg$_2$ crystal structures in the homogenization of elastic properties. Results are as follows:

(1) The calculated lattice parameters ($a$, $b$ and $c$), the independent elastic constants, mechanical properties and the elastic anisotropy factor $A$ are in very good agreement with the experimental literatures.

(2) The $G/B$ ratio of shear modulus to bulk modulus at 0GPa is 0.663, which indicates slight brittleness of CaMg$_2$ phase at zero pressure.

(3) For Y parameter, when $w^2=1/3$, $E$ is 46.05GPa, which is equal to the result of Hill model. Therefore, using Y parameter method to study elastic moduli of CaMg$_2$ phase is quietly feasible.

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References

[1] C. Potzies, K.U. Kainer, Advanced Engineering Materials, 6, 281-289 (2004).
[2] Z.B. Sajuri, T. Umehara, Y. Miyashita et al., Advanced engineering materials, 5, 910-916 (2003).
[3] B.Y. Tang, W.Y. Yu, X.Q. Zeng et al., Materials Science and Engineering: A, 489, 444-450 (2008).
[4] J.F. Nie, Scripta Mater. 48 (2003) 981.
[5] B.L. Mordike, T. Ebert, Materials Science and Engineering: A, 302, 37-45 (2001).
[6] K. Oh-Ishi, C.L. Mendis, T. Homma, S. Kamado et al., Acta Materialia, 57, 5593-5604 (2009).
[7] J.F. Fan, G.C. Yang, H. Xie, W.X. Hao, M. Wang, G.C. Yang, Y.H. Zhou, Mater. Trans. A 361 (2005) 235.
[8] P. Zhou and H. R. Gong, Journal of the mechanical behavior of biomedical materials, 8, 154-164 (2012).
[9] H. Zhang, S.L. Shang, Y. Wang, L.Q. Chen, Z.K. Liu, Intermetallics, 22 (2012) 17.
[10] Y. Ortega, M.A. Monge, R. Pareja, J. Alloys Compd., 463 (2008) 62.
[11] Y. Zhong, K. Qzturk, J.O. Sofo, Z.K. Liu, J. Alloys Compd. 420 (2006) 98.
[12] G. Yuan, Y. Liu, W. Ding, et al., Materials Science and Engineering: A, 474, 348-354 (2008).
[13] Y. Liu, G. Yuan, W. Ding, et al., Journal of alloys and compounds, 427, 160-165 (2007).
[14] W. Chen, J. Sun, Physica B: Condensed Matter, 382, 279-284 (2006).
[15] P. Zhou and H. R. Gong, Journal of the mechanical behavior of biomedical materials, 8, 154-164 (2012).
[16] K. Aono, S. Orimo, and H. Fujii., Journal of alloys and compounds, 309, L1-L4 (2000).
[17] W.Y. Yu, N. Wang, X.B. Xiao, B.Y. Tang et al., Solid State Sciences, 11, 1400-1407 (2009).
[18] Mao P, Yu B, Liu Z, et al., Journal of Magnesium and Alloys, 1, 256-262 (2013).
[19] Jia Fu, Fabrice Bernard, Siham Kamali-Bernard, Molecular Simulation, 44(4), 285-299 (2018).
[20] Jia Fu, K.-B. Siham, B. Fabrice, Marilyne Cornen, Compos Part B-Eng, 150, 1-15 (2018).
[21] Jia Fu, B. Fabrice, K.-B. Siham, J Phys Chem Solids, 101, 74-89 (2017).
[22] Jia Fu, B. Fabrice, K.-B. Siham, J Nano Res. 33, 92-105 (2015).
[23] Jia Fu, Weihui Lin, Zhongren Chen. IJAMP, 1(1), 62-69 (2016).
[24] Jia Fu, Weihui Lin, AER, 120, 390-395 (2017).
[25] M. J. P. Musgrave, Proc. Roy. Soc. (London) A226, 339(1954).
[26] J. R. Neighbours, J. Acoust. Soc. Am. 26, 865 (1954).
[27] Ali Sumer and J. F. Smith, Journal of Applied Physics 33, 2283 (1962).
[28] D. Raabe, Wiley-VCH, Weinheim,1998.
[29] Zheng, L., Min, L., Acta Physica Sinica, 58(12), 8511-8521 (2009).
[30] B. Xiao, J. Feng, C. T. Zhou, Y. H. Jiang and R. Zhou, J. Appl. Phys., 109, 023507 (2011).