Ab Initio Calculation on the Structure and Elastic Properties of a Magnesium-Lithium Alloy

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Lattice constants, bulk modulus and heat of solution of a Mg₇Li₁ alloy are calculated by using an *ab initio* pseudopotential method based on the density function theory and the supercell approach. Lattice constants and bulk modulus at zero pressure are obtained by using the stress calculation and generalized Hooke's law. For exchange and correlation method, the Wigner formula are used and the results are compared with ones using the Perdew and Zunger formula. Calculated lattice constants and bulk modulus are in good agreements with experimental values. We also calculate three kinds of ordered structures on this alloy in order to examine the influence of the structure. The results of three structures are different, respectively, and the influence is discussed from the atomic and electronic structure. The valence charge distribution is decreased around Li atoms. Especially, this region of the low charge distribution spreads in *c* direction.

(Received January 22, 2001; Accepted March 29, 2001)

Keywords: *ab initio*, magnesium, lithium, lattice constants, bulk modulus, heat of solution

1. Introduction

Magnesium is the lightest in the metal utilized industrially. If lithium that is a lighter element is added in magnesium, the alloy becomes lighter and higher specific strong than the pure metal of magnesium. Therefore, this Mg-Li alloys are expected as a structural material. A lot of experimental investigations on fundamental properties of the alloys are performed for a long time,¹⁻³⁾ however there are a few investigations by theoretical *ab initio* calculation.^{4,5)}

In the present work lattice constants and bulk modulus are calculated of Mg₇Li₁ alloy by using an *ab initio* pseudopotential method and the supercell approach. The calculated results are compared with experimental values. As Li has relatively high solid solubility in Mg (17.0 at%, 5.5 mass%), this Mg₇Li₁ alloy which contains 12.5 at% (3.9 mass%) Li is a solid solution of HCP geometry.

Ab initio calculation is an accurate way to know the electronic properties of matter and uses only the theory without experimental value, but the computational workload is very large. Therefore, ordered structures which are rare in nature, in other words small supercells that contain a few atoms are usually used for *ab initio* calculation of alloys.^{4,6)} On FCC and BCC alloys it may be small matter that lattice constants are calculated using such ordered structures because their structures are simple cubic and lattice constant is only one. However, on HCP alloys calculated lattice constants and axial ratio will be directly influenced by the structures. In the present work three kinds of ordered structures on Mg₇Li₁ alloy in order to examine the influence of the structure. Furthermore, the influence is discussed from the atomic and electronic structure.

The atomic configurations are optimized in each structure, and the motion of atoms is calculated by integration of the classical equation of motion subjected to Hellmann-Feynman

force. The optimization can relax Mg atoms around Li atoms in the alloy. Stable lattice constants and bulk modulus at zero pressure can be calculated by using the stress calculation and generalized Hooke's law. It is noted that all calculations are carried out on ground state in other words at 0K. Heat of solutions are also examined in order to discuss relative stability.

Similar calculation has been carried out on same Mg₇Li₁ alloy.⁵⁾ However, for exchange and correlation method it is used the Perdew and Zunger formula⁷⁾ parameterized the Ceperley and Alder results⁸⁾ and only two structures of Mg₇Li₁ alloy are examined. In the present work the Wigner formula⁹⁾ that is better for Mg, Li and Mg-Li alloy is used and three structures are examined adding another new structure. Calculated values approximate to experimental values very much by using the Wigner formula.

2. Method of Calculations

Mg₇Li₁ alloy is calculated with three structures of supercell A and B, C including 14 Mg atoms and 2 Li atoms (see Fig. 1). Their structures are different in the substitution sites of Li atoms. These supercells are divided into eight HCP unit cells. The θ is fixed at 120° in structure A. However, it is not in structure B and C because there is not symmetrical restriction and structure B and C are not HCP geometry exactly. The similar supercell with A is adopted in pure metals of Mg and Li.

The electronic structure calculation is based on the local density approximation (LDA) in the density function theory (DFT)^{10,11)} with the Wigner formula for the exchange and correlation method. The electronic ground state is efficiently obtained using the conjugate-gradient technique¹²⁾ with the Keker mixing scheme.¹³⁾ Stable atomic configurations are obtained through relaxation according to Hellmann-Feynman forces. The present scheme is very efficient for metallic large systems.¹⁴⁾

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Fig. 1 Three structures of supercell (a) A, (b) B and (c) C. Black and white spheres correspond to Mg and Li atoms, respectively.

For Mg, we use the TM-type pseudopotential.¹⁵⁾ For the pseudopotential generation, the configuration $3s^{1.5} 3p^{0.25} 3d^{0.25}$ is used. The cut off radii are 0.116, 0.127, and 0.127 nm for s , p , and d orbitals, respectively. For Li, we use the BHS-type pseudopotential.¹⁶⁾ The configuration $2s^{0.1} 2p^{0.05} 3d^{0.05}$ is used. The cut off radii are 0.101, 0.106, and 0.106 nm for s , p , and d orbitals, respectively. The p part is treated as a local potential for both Mg and Li, and the pseudopotentials are transformed to a separable form as suggested by Kleinman and Bylander.¹⁷⁾ The partial core correction¹⁸⁾ is included in the pseudopotential of Li.

The Kohn-Sham equation is solved self-consistently within a plane-wave basis. All plane waves with a kinetic energy less than a certain cut-off energy are included in the basis. In order to determine a proper value for this cut-off energy, the convergence of total energy for cut-off energy is examined. The cut-off energy of 4.36×10^{-17} J (272 eV) is sufficient for all our purposes and it is used in this paper. 32 special k points¹⁹⁾ per irreducible 24th of the Brillouine zone for structure A and pure metals are used. 74 special k points per irreducible 8th of the Brillouine zone for structure B and C are used. For fractional occupancies, we use the Gaussian broadening scheme²⁰⁾ with sigma of 3.2×10^{-20} J (0.2 eV).

Not only stable atomic configurations but also stable lattice constants at zero pressure are calculated. For this kind of problem, the BFGS method²¹⁾ is well used. This utilizes non-linear fit by quasi-Newton scheme. However, linear fit is convenient and effective in elastic deformation in order to calculate stable lattice constants. This linear fit is generalized Hooke's law concretely. In this method stresses must be calculated and it can be calculated by the *ab initio* pseudopotential method.²²⁾ If the shear stresses do not work, generalized Hooke's law is defined by

$$\begin{pmatrix} \sigma_X \\ \sigma_Y \\ \sigma_Z \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} \varepsilon_X \\ \varepsilon_Y \\ \varepsilon_Z \end{pmatrix}, \quad (1)$$

where σ_X , σ_Y and σ_Z are normal stresses in X , Y and Z direction, respectively. Strains ε_X , ε_Y and ε_Z are defined by

$$\begin{cases} \varepsilon_X = (X - X_0)X_0 \\ \varepsilon_Y = (Y - Y_0)Y_0 \\ \varepsilon_Z = (Z - Z_0)Z_0, \end{cases} \quad (2)$$

where X_0 , Y_0 and Z_0 are stable lattice constants making stresses all zero. From eq. (1),

$$\begin{pmatrix} \sigma_X - \sigma_X^* \\ \sigma_Y - \sigma_Y^* \\ \sigma_Z - \sigma_Z^* \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} \varepsilon_X - \varepsilon_X^* \\ \varepsilon_Y - \varepsilon_Y^* \\ \varepsilon_Z - \varepsilon_Z^* \end{pmatrix}. \quad (3)$$

If lattice constants X , Y and Z are nearly equal X_0 , Y_0 and Z_0 respectively, the following equation is approximately consistent.

$$\begin{cases} \varepsilon_X - \varepsilon_X^* = (X - X_0)X_0 - (X^* - X_0)X_0 \approx (X - X^*)X \\ \varepsilon_Y - \varepsilon_Y^* = (Y - Y_0)Y_0 - (Y^* - Y_0)Y_0 \approx (Y - Y^*)Y \\ \varepsilon_Z - \varepsilon_Z^* = (Z - Z_0)Z_0 - (Z^* - Z_0)Z_0 \approx (Z - Z^*)Z. \end{cases} \quad (4)$$

From eqs. (3) and (4),

$$\begin{pmatrix} \sigma_X - \sigma_X^* \\ \sigma_Y - \sigma_Y^* \\ \sigma_Z - \sigma_Z^* \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} (X - X^*)/X \\ (Y - Y^*)/Y \\ (Z - Z^*)/Z \end{pmatrix}. \quad (5)$$

All elastic constants are derived from eq. (5) by calculating stresses at adequate lattice constants. For example, X , Y and Z are decided as $Y = Y^*$ and $Z = Z^*$ in order derive elastic constants c_{11} , c_{21} and c_{31} .

$$\begin{pmatrix} \sigma_X - \sigma_X^* \\ \sigma_Y - \sigma_Y^* \\ \sigma_Z - \sigma_Z^* \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} (X - X^*)/X \\ 0 \\ 0 \end{pmatrix}. \quad (6)$$

As σ_X , σ_Y and σ_Z at X , Y and Z , and σ_X^* , σ_Y^* and σ_Z^* at X^* , $Y^* = Y$ and $Z^* = Z$ are calculated respectively by the *ab initio* pseudopotential method, it is possible that c_{11} , c_{21} and c_{31} are derived from eq. (6). Then, there are two cautions. First, the atomic configurations are sufficiently relaxed before stresses are calculated. Second, X^* is sufficiently near to X but the effects of error in calculated stresses increase when it is too near. Similarly, c_{12} , c_{22} and c_{32} are derived from calculated σ_X^* , σ_Y^* and σ_Z^* at $X^* = X$, Y^* and $Z^* = Z$, and c_{13} , c_{23} and c_{33} are derived from calculated σ_X^* , σ_Y^* and σ_Z^* at $X^* = X$, $Y^* = Y$ and Z^* . Stable lattice constants are predicted from obtained all elastic constants. In eq. (5) X^* ,

Table 1 Lattice constants and bulk modulus of Mg and Li. W is with the use of the Wigner formula and PW is with the use of the Perdew and Zunger formula. Calculated values are shown with the difference from experimental value in the parenthesis. Experimental value are also shown with the measured temperature in the parenthesis.

		W	PW ⁵⁾	Experiment
Mg	a (nm)	0.3148 (−1.9%)	0.3106 (−3.3%)	0.3211 ²⁾ (at 298 K)
	c (nm)	0.5135 (−1.4%)	0.5062 (−2.8%)	0.5210 ²⁾ (at 298 K)
	c/a	1.631 (+0.5%)	1.630 (+0.4%)	1.623 ²⁾ (at 298 K)
	B (GPa)	36.0 (+1.1%)	39.3 (+10.4%)	35.6 ³⁾ (at 298 K)
Li	a (nm)	0.3015 (−3.1%)	0.2962 (−4.8%)	0.3111 ²³⁾ (at 78 K)
	c (nm)	0.4930 (−3.2%)	0.4845 (−4.9%)	0.5093 ²³⁾ (at 78 K)
	c/a	1.635 (−0.1%)	1.636 (−0.1%)	1.637 ²³⁾ (at 78 K)
	B (GPa)	13.3 (+4.7%)	14.3 (+12.6%)	12.7 ²⁴⁾ (at 4 K)

Y^* and Z^* are replaced with X_0 , Y_0 and Z_0 , respectively.

$$\begin{pmatrix} \sigma_X - 0 \\ \sigma_Y - 0 \\ \sigma_Z - 0 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} (X - X_0)/X \\ (Y - Y_0)/Y \\ (Z - Z_0)/Z \end{pmatrix}, \quad (7)$$

where these have already been proven except for X_0 , Y_0 and Z_0 , and eq. (7) is solved for this provisional X_0 , Y_0 and Z_0 that are predicted as stable. Actually the stresses do not become all zero at predicted X_0 , Y_0 and Z_0 . Therefore, predicted X_0 , Y_0 and Z_0 are made to be new X , Y and Z , and above mentioned calculation are repeated. This cycle are repeated until X_0 , Y_0 and Z_0 are converged. We obtain converged X_0 , Y_0 and Z_0 within three cycles using experimental values as first X , Y and Z .

Above mentioned method is for structure B and C that lattice constants X , Y and Z are independent, respectively. In structure A and pure metals, $X = Y$ and $\sigma_X = \sigma_Y$ are consistent. Therefore, Hooke's law is redefined by

$$\begin{pmatrix} \sigma_X \\ \sigma_Z \end{pmatrix} = \begin{pmatrix} c_{11} + c_{12} & c_{13} \\ 2c_{31} & c_{33} \end{pmatrix} \begin{pmatrix} \varepsilon_X \\ \varepsilon_Z \end{pmatrix}. \quad (8)$$

Similarly, stable lattice constants $X_0 = Y_0$ and Z_0 are able to be obtained.

In structure B and C bulk modulus B is given by

$$B = \frac{c_{11} + c_{21} + c_{31} + c_{12} + c_{22} + c_{32} + c_{13} + c_{23} + c_{33}}{9}, \quad (9)$$

and in structure A and pure metals

$$B = \frac{2c_{11} + 2c_{12} + 2c_{13} + 2c_{31} + c_{33}}{9}, \quad (10)$$

where all elastic constants are determined from liner least-squares fit of stress as a function of strain. For this calculation eight supercells that are strained from -0.125% to $+0.125\%$ are employed.

The heat of solution ΔH of Li in Mg defined by

$$\Delta H = N_A \left(\frac{1}{2} E[\text{Mg}_{14}\text{Li}_2] - \frac{7}{16} E[\text{Mg}_{16}] - \frac{1}{16} E[\text{Li}_{16}] \right), \quad (11)$$

where N_A is Avogadro's number and $E[\text{Mg}_{14}\text{Li}_2]$ is the total energy per a supercell of the alloy with stable lattice constants and atomic configurations. $E[\text{Mg}_{16}]$ and $E[\text{Li}_{16}]$ are the total energies of Mg and Li, respectively. This heat of solution is

the energy necessary for substituting 1 mol Li in 7 mol Mg at 0 K and the entropy is not contained. The negative energies mean the exothermic reaction, and the positive ones mean the endothermic reaction, respectively.

3. Results and Discussions

It is required to describe the exchange and correlation energy using approximation method in *ab initio* calculation based on the DFT. The simplest method of describing the exchange and correlation energy is to use the LDA, and this approximation is almost universally used in *ab initio* calculation. In the LDA the exchange and correlation energy of an electronic system is assumed to be equal the exchange and correlation energy in a homogeneous electron gas that has same electronic density. Several parameterizations exist for the exchange and correlation energy of a homogeneous electron gas. The Perdew and Zunger formula and the Wigner formula are used well for this exchange and correlation method. In the present work the Wigner formula are used. The calculated equilibrium lattice constants and the bulk modulus on pure metals of Mg and Li are shown in Table 1. This table also includes the cited calculated values⁵⁾ using the Perdew and Zunger formula and the available experimental values. In the present work all results are calculated at 0 K. It is difficult that calculated values are directly compared with experimental values, because some experimental values are measured at room temperature. As Li of HCP geometry is more stable than that of BCC geometry at low temperature, the cited experimental values of Li are that of HCP geometry. The condition of the cited calculation is same except for the exchange and correlation method. The exchange and correlation method influences the results cleanly. The values using the Wigner formula approximate to the experimental values on both Mg and Li further than using the Perdew and Zunger formula. Especially, the bulk modulus drastically approximate to experimental values. Therefore, the Wigner formula is also chosen for the alloy. The difference between calculated values and experimental values is remained, and it is mainly due to the LDA itself.

Calculated lattice constants, bulk modulus and heat of solution of the alloy are shown in Table 2. This table also includes the cited calculated values⁵⁾ of structure A and B using the Perdew and Zunger formula and the value derived from liner least-squares fit of experimental value.^{2,3)} The values using

Table 2 Lattice constants, bulk modulus and heat of solution of structure A, B and C. W is with the use of the Wigner formula and PW is with the use of the Perdew and Zunger formula. Calculated values are shown with the difference from experimental value in the parenthesis. It is also shown the value derived from liner least-squares fit of experimental values measured at 298 K.

	a (nm)	c (nm)	c/a	θ	B (GPa)	ΔH (KJ/mol)
A (W)	0.3144 (−2.0%)	0.5031 (−2.7%)	1.600 (−0.8%)	120°	32.7 (−3.4%)	−12.3
B (W)	0.3138 (−2.2%)	0.5043 (−2.5%)	1.607 (−0.4%)	119.94°	33.0 (−2.5%)	−13.6
C (W)	0.3145 (−2.0%)	0.5023 (−2.9%)	1.597 (−1.0%)	119.95°	32.2 (−4.9%)	−13.1
A (PW) ⁵⁾	0.3100 (−3.4%)	0.4956 (−4.2%)	1.599 (−0.9%)	120°	36.1 (+6.6%)	−12.5
B (PW) ⁵⁾	0.3095 (−3.5%)	0.4969 (−3.9%)	1.605 (−0.4%)	119.96°	35.9 (+6.0%)	−14.5
Experiment	0.3208 ²⁾	0.5173 ²⁾	1.613 ²⁾	—	33.9 ³⁾	—

Fig. 2 Axial ratio c/a of Mg-Li alloys vs. Li concentration in at%. It is also shown available experimental values measured at 298 K.

the Wigner formula approximates to experimental value even in the alloy as well as the pure metals and they are in good agreements with experimental values.

Calculated heat of solution is negative value and this is in agreement with that real Mg_7Li_1 alloy is a solid solution. As the structure is more stable as heat of solution is lower, structure B is most stable and realistic to the real structure of Mg_7Li_1 alloy in structure A, B and C.

Calculated lattice constants of three structures are different a little, respectively. Axial ratios c/a of the Mg-Li alloys are shown in Fig. 2 as a function Li concentration. All calculated axial ratio are smaller than experimental value. Especially, axial ratio of structure C is smallest. It is concerned with the atomic and electronic structure. The valence charge distribution on (0001) plane of structure A is shown in Fig. 3, and it is decreased around Li atoms. The low charge distribution around Li atom is not simply spherical but triangular. The similar charge distribution is also confirmed in structure B and C. The valence charge distribution on (11 $\bar{2}$ 0) plane of structure A, B and C is shown in Fig. 4. The region of the low charge distribution around Li atom spreads in c direction and it is like triangular prism three-dimensionally. Therefore, lattice constants tend to decrease naturally in c direction than a

Fig. 3 The valence charge distribution on (0001) plane of structure A.

direction. Especially, Li atoms in structure C are stacking orderly in c direction, and so lattice constant c decreased most. In the contrary, in structure B Li atoms stacks are not ordered very much in c direction and the axial ratio approximates to experimental value most. The structure of real Mg_7Li_1 alloy seems to be disordered or long range ordered, and so the experimental axial ratio is larger than the all calculated axial ratios.

Figure 5 shows bulk modulus of the Mg-Li alloys as a function Li concentration. It also shows available experimental values which are derived from referenced elastic constants by using eq. (10). It well reproduces that bulk modulus of the Mg-Li alloy decrease with increasing the concentration of Li by the calculation. The bulk modulus is also influenced by the structure of the alloys and in structure B it approximates to experimental value most.

Structure B is most appropriate for Mg_7Li_1 alloy in three structures because it is the most stable structure and both axial ratio and bulk modulus are approximate to experimental values most. However, structure B is not always real structure of this alloy. On *ab initio* calculation of alloys with supercell, it is important that not only calculation method like the exchange and correlation method but also influence of the structure of alloys in order to calculate accurate lattice constants and bulk modulus.

4. Summary

Lattice constants and bulk modulus of Mg_7Li_1 alloy are calculated by using the *ab initio* pseudopotential method and

Fig. 4 The valence charge distribution on $(11\bar{2}0)$ plane of structure (a) A, (b) B and (c) C.

Fig. 5 Bulk modulus B of Mg-Li alloys vs. Li concentration in at%. It is also shown available experimental values measured at 298 K.

the supercell approach. For the exchange and correlation method, the Wigner formula are used and the results are compared with ones using the Perdew and Zunger formula. In the present work the Wigner formula is better for Mg, Li and Mg-Li alloy. The calculated results are in good agreements with experimental values. Three kinds of structures are calculated in order to examine the influence of the structure of the alloy. The results of three structures are different a little, respectively. The difference of axial ratio is owing to ordered structure and the electronic structure that the charge distribution around Li atoms decreased in c direction. On *ab initio* calculation of alloys with supercell, the structure of alloy is important that in order to calculate accurate lattice constants and bulk modulus.

Acknowledgment

We are grateful to the financial support of “the Priority Group of Platform Science and Technology for Advanced Magnesium Alloys, Ministry of Culture, Science and Education” (11225209) and “The Light Metal Educational Foundation Inc.”.

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