A first principles study on the structure and the elastic properties of Li-Mg alloys

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P T Salo and K Kokko

Department of Physics, University of Turku, SF-20500 Turku, Finland

Abstract. Elastic properties of the $Li_{15}Mg$ alloy have been studied by using the first principles structural optimization method. The results show that at zero pressure the relative distance between the Mg atom and the nearest Li atoms is larger than that in the ideal crystal and when compressing the lattice this distance will increase further. A simple model is introduced to interpret this relaxation. It is also shown that structural optimization has to be taken into account when investigating the bulk properties of alloys. The bulk modulus of the optimized $Li_{15}Mg$ is smaller than that of the ideal structure although the volume of the optimized structure is smaller than the volume of the ideal structure. Hence bulk modulus is determined not only by change in the crystal volume but also by local changes in the crystal structure near to the Mg atom. An interpolation formula to calculate compressibility at any composition is presented.

1. Introduction

In recent years a number of experimental and theoretical investigations have been performed on Li–Mg alloys. These alloys are technologically promising due to their low density and high stiffness. Because of their nearly free electron character and high solubility (up to 70 at.% Mg in BCC Li), Li–Mg alloys serve as an ideal test system for comparison between experiments and theoretical models of alloying.

Mason *et al* [1] have studied Mg–Li alloys as a matrix for several fibrous composites. The very high chemical reactivity and diffusional mobility of Li makes these systems both interesting and difficult in composite production. González-Doncel *et al* [2] have studied a foil metallurgy processing technique for preparing two-phase Mg–9Li laminates and Mg–9Li–5B$_4$C composites. The specific stiffness values of these materials are shown to be higher than those of most commercial aluminium and titanium alloys. Vaks and Trefilov [3] have made model calculations for disordered $Li_{1-x}Mg_x$ in order to estimate the effects of singularities in the electron density of states on elastic and thermodynamic properties of alloys.

In the present work elastic properties of Li–Mg alloys have been studied by using the first principles molecular dynamics method. The molecular dynamics calculation enables us to optimize the crystal structure, which makes it possible to investigate how lattice relaxation around Mg atoms affects lattice constant and bulk modulus.

The purpose of the present study is to provide some theoretical results for Li–Mg alloys and discuss their implications in order to achieve a better understanding of the elastic properties of alloys in general. The structural optimization (SO) calculations will show how the Li atoms relax around the Mg atom in $Li_{15}Mg$ and how the $Li_{15}Mg$ alloy behaves under

hydrostatic pressure. Furthermore, the possibility of predicting the bulk modulus of an alloy by using the data of pure components is discussed.

2. Method and calculations

The calculations for Li_{16} and $Li_{15}Mg$ have been made with simple cubic (SC) geometry (figure 1). The calculations for pure Li and Mg have been made with BCC geometry.
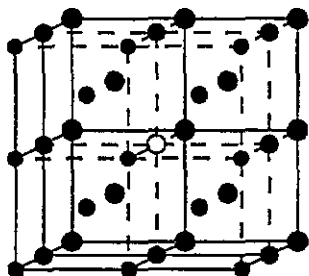

Figure 1. The supercell of $Li_{15}Mg$ alloy is made up of eight conventional BCC cells. Black and white spheres correspond to Li and Mg atoms, respectively.

The electronic structure calculation is based on the local density approximation in the density functional theory [4, 5] with the Wigner interpolation formula [6] for the exchange and correlation. A norm-conserving pseudopotential is obtained by following the prescription of Bachelet *et al* [7], except that *p* and *d* pseudopotentials are obtained by Hamann's scheme [8]. The *d* part is treated as a local potential and the pseudopotentials are transformed to a separable form as suggested by Kleinman and Bylander [9]. Partial core correction [10] is included in the pseudopotentials of both Li and Mg [11].

The optimization of the electronic and ionic degrees of freedom is performed by a modified version of the first principles molecular dynamics [12]. The steepest descent type of algorithm for the electronic degrees of freedom has been adopted [13]. The ordinary molecular dynamics with the Hellmann–Feynman forces is used for the ionic motion. More details of the method are described in [11, 14].

The Schödinger equation is solved self-consistently within a plane-wave basis. All plane waves with an energy less than a certain cut-off energy (E_{cut}) are included in the basis. In order to determine a proper value for this cut-off energy the total energy and the forces acting on the atoms, fixed at their ideal BCC positions (figure 1), have been calculated as a function of E_{cut} (figure 2). In the following the cut-off energy of the plane-wave basis $E_{cut} = 12.25$ Ryd is used because this value seems to give converged results for the forces and the total energies. The same kind of procedure was also done for the total number of *k*-points (figure 2). In the calculations we use 35 inequivalent *k*-points in the irreducible wedge of the SC Brillouin zone. In our procedure the convergence criterion for forces acting on atoms is 1.0 mRyd/a_0 (a_0 is the Bohr radius).
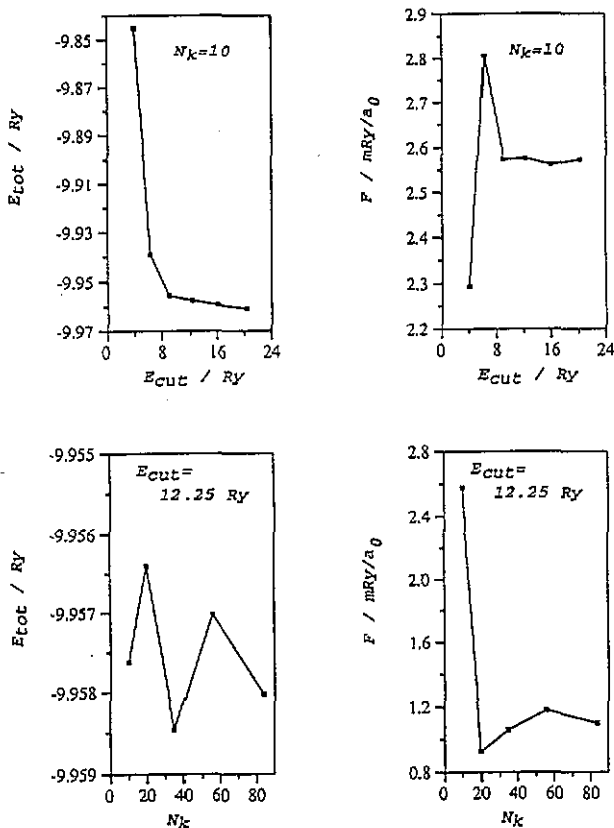
Figure 2. The total energy of $Li_{15}Mg$ and the existing forces. Both quantities are shown as a function of the cut-off energy (E_{cut}) and the number of k-points (N_k). Force (F) is the absolute value of force acting on Li atoms inside the supercell.

3. Results and discussion

The total energy of Mg has been calculated with seven different lattice constants and the total energies of Li_{16} and $Li_{15}Mg$ with five different lattice constants in the neighbourhood of the minimum energy. After having done the fit presented by Banerjea and Smith [15] we calculated the equilibrium lattice constant and the bulk modulus from the obtained total energy curve. The structure of the $Li_{15}Mg$ alloy is optimized by allowing the atoms to move according to the forces in the SO calculation. In order to elucidate the structural relaxation a calculation has also been made for the ideal structure without the SO calculation. The equilibrium lattice constants and the bulk moduli are shown in table 1 which also includes the available experimental data [16, 17]. The calculated equilibrium lattice constant for Mg is 1% below the experimental value and the bulk modulus is about 5% below the experimental result. For Li_{16} the corresponding result for the equilibrium lattice constant is 3% below and for the bulk modulus about 20% above the experimental values. The equilibrium lattice constant of (optimized) $Li_{15}Mg$ is only 0.04% below the value of Li_{16} but the bulk modulus of $Li_{15}Mg$ is 8% larger than that of Li_{16}.

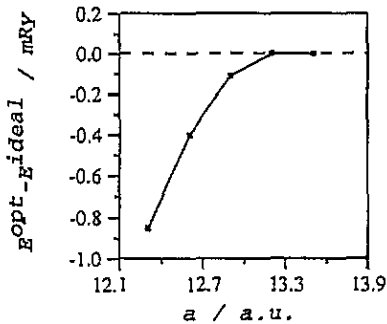Table 2 shows the average atomic volumes of $Li_{1-x}Mg_x$ alloy obtained by the present SO

Table 1. The equilibrium lattice constant and the bulk modulus of Mg, Li_{16} and Li_{15}Mg. There are two values for Li_{15}Mg, one for the ideal (I) and the other for the optimized structure (II). The values for Mg are calculated with BCC geometry and the others are calculated with SC geometry. The experimental lattice constant for Mg is transformed to the BCC structure by using the values of HCP structure ($a = 6.065$ au and $c = 9.847$ au [16]), so that the atomic volume does not change. The experimental lattice constant for Li_{16} is twice the experimental value for Li [16].

	a_{calc} (au)	$a_{expt}^{[16]}$ (au)	B_{calc} (Mbar)	$B_{expt}^{[17]}$ (Mbar)
Mg	6.728	6.795	0.339	0.354
Li_{16}	12.876	13.263	0.138	0.116
Li_{15}Mg (I)	12.877	—	0.151	—
Li_{15}Mg (II)	12.871	—	0.149	—

calculation and by a model calculation by Vaks and Trefilov. The model calculation gives a positive slope for $\Omega = \Omega(x)$ while the present calculation predicts a slightly negative slope, in agreement with experiment [16]. The calculation for the unoptimized structure (atoms at their ideal BCC positions) gives a slightly positive value for the slope above (see table 1). The structural optimization decreases the total energy of an alloy (see figure 3) and when the lattice parameter is decreased the difference between the energies of the optimized and ideal structures increases. This is why in this case the equilibrium lattice parameter (and volume) decreases from its ideal BCC structure value. All this shows the importance of structural optimization when investigating bulk properties of alloys under compression.

Table 2. Average atomic volume in $Li_{1-x}Mg_x$ alloy. The values Ω_{VT} by Vaks and Trefilov are taken from figure [3].

at.% Mg	Ω_{calc} (au^3)	$\Omega_{VT}^{[3]}$ (au^3)	$\Omega_{expt}^{[16]}$ (au^3)
0.00	133.4	142.0	145.9
6.25	133.3	143.1	—
15.0	—	—	144.5

Figure 3. The difference between the total energies of the optimized and ideal structures of the Li_{15}Mg alloy.

In the course of the SO calculations the first eight neighbouring Li atoms of the Mg atom will relax from their original positions when the forces are acting, while the others
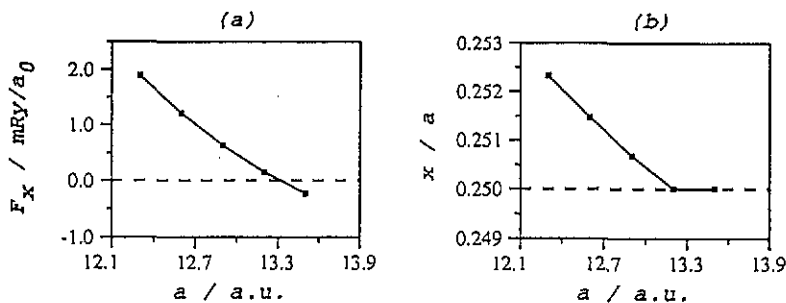
Figure 4. Li$_{15}$Mg alloy: the x component of force acting on the nearest-neighbour Li atom in the ideal structure (a) and the relative distance between the Mg atom and the nearest Li atoms in the optimized structure (b) as a function of the lattice constant.

will remain in their original positions, according to symmetry requirements. In figure 4 the forces in the ideal structure and the relative position of the first neighbours of the Mg atom in the optimized structure are shown. The present calculations show that at zero pressure the relative distance between the Mg atom and the nearest Li atoms is larger than that in the ideal crystal and when pressure (P) is increased the crystal structure of Li$_{15}$Mg will relax from its zero-pressure structure. In order to analyse this pressure-dependent relaxation we consider a simple model based on the properties of pure metals [18]. Bulk modulus (B) is defined as

$$B = -V \frac{\mathrm{d}P}{\mathrm{d}V}\bigg|_{V=V_0} \tag{1}$$

where V_0 is equilibrium volume. During compression the change in pressure in Li and Mg subsystems should be the same, which leads to an equation for the relative change in atomic volumes (Ω_i) in Li$_{15}$Mg under compression:

$$\frac{\mathrm{d}\Omega_{\mathrm{Mg}}}{\mathrm{d}\Omega_{\mathrm{Li}}} = \frac{\Omega_{\mathrm{Mg}}}{\Omega_{\mathrm{Li}}} \frac{B_{\mathrm{Li}}}{B_{\mathrm{Mg}}}. \tag{2}$$

The following qualitative prediction for the Li$_{15}$Mg system investigated is obtained. If the value of equation (2) is less (greater) than unity, then the first neighbouring Li atoms of the Mg atom will move relatively outwards from (towards) the Mg atom. The calculated value on the right-hand side of equation (2) is 0.5, which implies that the eight nearest Li atoms will shift relatively outwards from the central Mg atom as pressure is increased. This predicted pressure-dependent relaxation is indeed confirmed by the present SO calculations (see figure 4(b)). Research on other alloys (Li–Na and Li–Al) is in progress and results will be published later.

After obtaining bulk modulus (or compressibility $C = 1/B$) for the Li–Mg alloy at one composition a question arises whether it is possible to estimate bulk modulus for other compositions without performing additional electronic structure calculations. Varotsos [19] has calculated the bulk modulus of KCl$_{1-x}$Br$_x$ compound by using the data of pure solvent and solute only. Grammatikakis *et al* [20] have calculated the compressibility of alloys by using the data of pure solvent and an alloy at a single composition. They obtained a linearized model for dilute alloys which shows that the compressibility upon alloying is not

determined solely by change in volume (v^d) but by the product $v^d\,(C^d - C_0)$, where C^d and C_0 are the compressibilities of v^d and the pure solvent, respectively. This might shed some light onto experimental results such as where compressibility is increased upon alloying although the volume of the alloy is decreased, a fact that has been considered somewhat puzzling. In our calculations the bulk modulus of the optimized $Li_{15}Mg$ is smaller than that of the ideal structure although the volume of the optimized structure is smaller than the volume of the ideal structure. Hence local changes in the crystal structure near to the Mg atom will also contribute to bulk modulus.
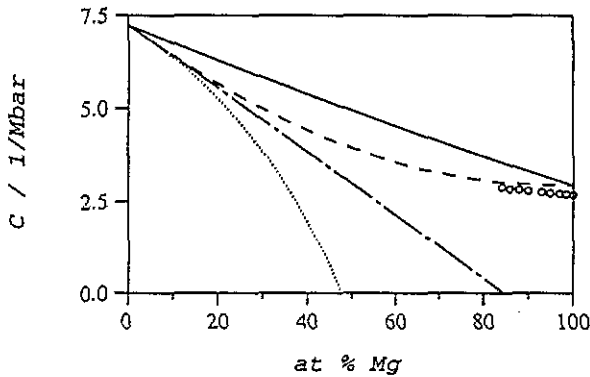

Figure 5. The compressibility of Li–Mg alloys as a function of at.% Mg. Shown are the diagrams calculated by using the model of Varotsos [19] (full curve), the model of Grammatikakis *et al* [20]: general form (chain curve) and linearized (with respect to N_2/N_1) form (dotted curve); and calculated from equations (3) and (4) (broken curve). The open circles are the experimental values [21].

As shown in figure 5, the models of Varotsos and Grammatikakis *et al* have limited validity in the case of Li–Mg alloys. Because of this, a combination of these two models has been introduced and tested for Li–Mg alloys [18]. In this combined model we can write for the volume of an alloy containing N_1 solvent and N_2 solute atoms

$$V_{N_1+N_2} = \frac{N_1}{N_1 + N_2}[N_1\Omega_1 + N_2(v_2^d + \Omega_1)]$$

$$+ \frac{N_2}{N_1 + N_2}[N_2\Omega_2 + N_1(v_1^d + \Omega_2)] \tag{3}$$

where Ω_i is the atomic volume of the pure component i and v_i^d is the change in the volume due to the replacement of one atom in a host crystal by a solute atom of type i. By rearranging the terms in equation (3) and then differentiating the obtained equation with respect to pressure we obtain an equation for compressibility of an alloy:

$$CV_{N_1+N_2} = \frac{1}{N_1 + N_2}[N_1^2 C_1\Omega_1 + N_2^2 C_2\Omega_2 + N_1 N_2(C_t^d\,v_t^d + C_1\Omega_1 + C_2\Omega_2)] \tag{4}$$

where $v_t^d = v_1^d + v_2^d$, C_i is the compressibility of pure crystal of type i and C_t^d is the compressibility of change in volume v_t^d. Figure 5 shows that, unlike the models

of Grammatikakis *et al* , this combined model gives positive compressibility for all compositions. It is obvious that this model gives correct compressibilities (i.e. the same values that are used in input data) for pure metals and good estimates for dilute alloys. In figure 5 some experimental data for the compressibility of Li–Mg alloys are also shown [21]. However, because the experimental data are for HCP alloys and the calculated data for BCC alloys the comparison of these two is not straightforward. Nevertheless, the calculated results evidently show the general behaviour for compressibility because the BCC structure is fairly similar to the HCP structure.

4. Summary

The first principles pseudopotential method is an accurate and convenient way of calculating the valence electron properties of matter. Also, the convergence is faster in the difference of quantities than in the quantities themselves. That is why quantities like, for example, pressure and bulk modulus that are determined by the difference of the total energy are expected to have a good convergence. To interpret the calculated results two simple models have been discussed. With one model we can describe how lattice relaxation will be changed under pressure and with the other we can estimate compressibility for any alloy composite when the compressibilities of pure metals and one composition are known.

The calculations show that when Mg is alloyed in Li the nearest Li atoms will shift slightly away from the Mg atom and when pressure is increased this shift is enhanced. The present structural optimization calculation predicts a slightly negative slope for the average atomic volume $\Omega = \Omega(x)$ for dilute $Li_{1-x}Mg_x$ alloys, in agreement with experiment. On the other hand, the results for the unoptimized structure give a slightly positive value for this slope. This shows the importance of structural optimization when investigating bulk properties of alloys. Further investigations are, however, needed for different Li-based alloys to get more systematic knowledge of the effects of alloying. Such calculations are already in progress by the authors.

Acknowledgments

References

[1] Mason J F, Warwick C M, Smith P J, Charles J A and Clyne T W 1989 *J. Mater. Sci.* **24** 3934–46
[2] González-Doncel G, Wolfenstine J, Metenier P, Ruano O A and Sherby O D 1990 *J. Mater. Sci.* **25** 4535–40
[3] Vaks V G and Trefilov A V 1988 *J. Phys. F: Met. Phys.* **18** 213–35
[4] Hohenberg P and Kohn W 1964 *Phys. Rev.* B **136** 864–71
[5] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133–8
[6] Wigner E 1934 *Phys. Rev.* **46** 1002
[7] Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev.* B **26** 4199–228
[8] Hamann D R 1989 *Phys. Rev.* B **40** 2980–7
[9] Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425–8

[10]   Louie S G, Froyen S and Cohen M L 1982 *Phys. Rev.* B **26** 1738–42
[11]   Kobayashi K, Morikawa Y, Terakura K and Blügel S 1991 *Tech. Rep. of ISSP, University of Tokyo* A 2454
[12]   Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471–4
[13]   Williams A R and Soler J 1987 *Bull. Am. Phys. Soc.* **32** 562
[14]   Kobayashi K 1990 *PhD thesis, University of Tokyo*
[15]   Banerjea A and Smith J R 1988 *Phys. Rev.* B **37** 6632–45
[16]   Pearson W B 1958 *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Belfast: Pergamon)
[17]   Kittel C 1976 *Introduction to Solid State Physics* 5th edn (New York: Wiley)
[18]   Salo P T and Kokko K 1992 *Report Series, Department of Physics, University of Turku* R 11
[19]   Varotsos P 1980 *Phys. Status Solidi* b **99** K93–6
[20]   Grammatikakis J G, Eftaxias K, Patapis S and Hadjicontis V 1988 *J. Phys. Chem. Sol.* **49** 965–7
[21]   Wazzan A R and Robinson L B 1967 *Phys. Rev.* **155** 586–94