Orbital-free density functional theory calculations of the properties of Al, Mg and Al–Mg crystalline phases

Karin M Carling[1] **and Emily A Carter**[2]

[1] Department of Applied Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden
[2] Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, CA 90095-1569, USA

E-mail: carling@fy.chalmers.se and eac@chem.ucla.edu

Abstract

We have used density functional theory in an orbital-free, implementation to calculate the properties of pure fcc Al, hcp and bcc Mg, and the meta-stable alloy phase β'' (Al$_3$Mg). Five linear-response-based kinetic energy density functionals have been used, one of which has a density-dependent (DD) response kernel. We demonstrate that orbital-free density functional theory (OF-DFT) can produce physically accurate properties for Al–Mg alloys, if the kinetic energy density functional employed has a DD-kernel.

1. Introduction

Aluminium–magnesium alloys are among the most familiar metallic materials, commercially used as wrought and casting alloys. Those with 1–5 wt% Mg are used as wrought alloys, while those with 5–10 wt% Mg are used as casting alloys. In general, both wrought and casting alloys are used without precipitation treatment. The good ductility of, e.g. Al-10 wt% Mg casting alloys comes from solution treatment, but natural ageing decreases ductility and increases the risk of stress corrosion cracking. This natural degeneration, age-hardening, of the material arises from the decomposition of the solid solution.

For temperatures around and below room temperature, the decomposition process of Al–Mg alloys is a four-stage sequence [1–7]:

$$\text{solid solution} \rightarrow \text{GP zones} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta.$$

The GP zones are believed to be plate-shaped clusters [8] with higher Mg content than the surrounding matrix, and they do not contribute to age-hardening [1]. The β'' phase, sometimes designated as ordered GP zones [8], is believed to form from the GP zone clusters, and has the composition Al$_3$Mg in the L1$_2$ structure. Formation of β'' precipitates will affect the ductility of the alloy. Both GP zones and β'' are precipitates that have coherent interfaces with the

surrounding matrix, and they nucleate homogeneously from the solid solution. The β' phase has semi-coherent interfaces with the matrix, and has a hexagonal structure with a composition of approximately Al_3Mg_2. The final phase, the stable β, has a complex α-Mn structure with more than 1100 atoms in the unit cell [9], and the composition is Al_3Mg_2. The nucleation of β' and β precipitates is mainly a heterogeneous process at dislocations and grain boundaries. Both β' and β precipitation will have profound effects on the hardness of the material, as well as the risk of corrosion cracking.

To investigate the first stages of the degeneration process, characterization of the properties of the GP zone and β'' phases is a natural starting point. The β'' phase has a well characterized structure and composition, and coherent interfaces with the surrounding fcc lattice of Al. Therefore, this phase is attractive for testing the accuracy of first-principles theories, via calculation of its lattice parameter, bulk modulus, formation energy and other properties. Also, the Mg content needed for the precipitation of GP zone and β'' phases is quite high, which makes it difficult to separate the structure of these phases from the statistical clustering of Mg atoms. The present calibration study may be viewed as a first step towards investigating the properties of small Mg clusters in Al–Mg alloys with first-principles techniques.

Traditional first-principles methods, such as the density functional theory (DFT) [10, 11], often produce very good results. In the Kohn–Sham (KS) formulation [11], the intrinsic errors are limited primarily to the approximate evaluation of electron exchange and correlation, errors that often are reasonably small in condensed matter systems. However, these methods are very computationally demanding. The introduction of the KS orbitals yields an $O(N^3)$ scaling due to the orthonormality constraints on these orbitals. The calculational expense rises even further for metals, compared with other materials, due to the need for a dense set of k-points sampling the Brillouin zone in order to define the Fermi surface correctly, and to obtain the electronic potential and total energy accurately [12]. This poor scaling (multiplied by a prefactor containing the number of k-points) makes the KS formulation of DFT unsuitable for large scale calculations, such as those that would be required to study, e.g. the β (Al_3Mg_2) phase or dilute metal alloys including hundreds to many thousands of atoms in the simulation cell. Therefore, linear scaling methods are very attractive, particularly if we desire to investigate a large number of metal atoms, e.g. at a grain boundary or a precipitate. One approach to linear scaling is to exploit the locality of the system's electronic wavefunctions [13], but this is not feasible for metals, where the electronic interactions are long-ranged.

The orbital-free density functional theory (OF-DFT), an alternative linear scaling approach that does work for metals, begins with the original Hohenberg–Kohn formulation [10] of the DFT, which states that the electron density uniquely determines the ground-state total energy. In this approach, all terms in the total energy are expressed as functionals of the electron density alone; no orbitals are employed. The advantage of this technique is the $O(N \ln N)$ scaling of the algorithm for any system size (i.e. there is no crossover between $O(N^3)$ and $O(N)$ as there is in all other linear scaling schemes), and the avoidance of Brillouin zone sampling, which saves an enormous expense associated with orbital-based DFT calculations on metals. The central challenge in this OF-DFT is to find an appropriate density functional for the (non-interacting) kinetic energy, which in KS theory is calculated exactly via the KS orbitals. So far, a general, numerically practical, and transferable kinetic energy functional has not been developed, although there has been some progress during the last decades [14], especially for nearly-free-electron-like main group metals [15–20].

To reduce the computational effort of DFT calculations, it is common to treat only the valence electrons explicitly. The combined effect of the nucleus and core electrons of an atom is modelled with a pseudopotential. In the OF-DFT only local pseudopotentials (LPPs) can be used since there are no orbitals available for separation of the potentials for

different angular momenta, i.e. non-local pseudopotentials (NLPPs). Today, reliable LPPs have only been derived for a handful of nearly-free-electron-like metals, e.g. Na, Mg, and Al. A comprehensive set of LPPs needs to be developed to make OF-DFT useful for a wider variety of elements [21–23]. Recently, a method for deriving *ab initio* LPPs has been developed [24].

In this paper, we have tested the performance of some kinetic energy density functionals for OF-DFT calculations on the β'' phase of the Al–Mg alloy, as well as the pure elements. In section 2, we explain some of the basics of OF-DFT, and in section 3, the calculational details are stated. Our results are presented in section 4, and they are discussed in section 5. In section 6, we present conclusions.

2. Kinetic energy functionals

A family of kinetic energy density functionals, which are meant to approximate the non-interacting KS kinetic energy, has been developed in the last decade. These functionals are constructed to produce the correct linear response behaviour, as given by the Lindhard response function [25] for the non-interacting electron gas, to small changes in the external potential. The inclusion of proper linear response will introduce the important, long range, Friedel oscillations. Also, all of these functionals possess some subset of the following properties:

(a) In the limit of a uniform electron gas, the functional should reduce to the Thomas–Fermi functional [26, 27], T_{TF}, which is exact in this limit.
(b) For a slowly varying density, where the wave-vector $q \to 0$, the functional should reduce to the conventional gradient expansion (CGE) [28].
(c) For a single-orbital system, the functional should reduce to the von Weizsäcker functional, T_{vW} [29].
(d) For a rapidly varying density, $q \to \infty$, the functional should reduce to $T_{\mathrm{vW}} - \frac{3}{5}T_{\mathrm{TF}}$, i.e. the correct large-q limit [19].

The linear response kinetic energy functionals can be written generally as

$$T_{\mathrm{s}}[n(\boldsymbol{r})] = T_{\mathrm{TF}}[n(\boldsymbol{r})] + T_{\mathrm{vW}}[n(\boldsymbol{r})] + T_{\mathrm{X}}[n(\boldsymbol{r})], \tag{1}$$

where $n(\boldsymbol{r})$ is the density, $T_{\mathrm{TF}}[n(\boldsymbol{r})]$ is the Thomas–Fermi functional, and $T_{\mathrm{vW}}[n(\boldsymbol{r})]$ is the von Weizsäcker functional. The last term, $T_{\mathrm{X}}[n(\boldsymbol{r})]$, is formulated to introduce the correct linear response behaviour, although the form for this functional is not unique. A general expression for $T_{\mathrm{X}}[n(\boldsymbol{r})]$ can be deduced by rewriting $T_{\mathrm{TF}}[n(\boldsymbol{r})]$ and $T_{\mathrm{vW}}[n(\boldsymbol{r})]$ in the double integral form [20]:

$$\begin{aligned} T_{\mathrm{TF}}[n(\boldsymbol{r})] &= \frac{3}{10}(3\pi^2)^{2/3} \int n^{5/3}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} \\ &= \frac{3}{10}(3\pi^2)^{2/3} \iint n^{5/6}(\boldsymbol{r})\delta(\boldsymbol{r} - \boldsymbol{r}')n^{5/6}(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \end{aligned} \tag{2}$$

and

$$\begin{aligned} T_{\mathrm{vW}}[n(\boldsymbol{r})] &= \frac{1}{8} \int \frac{|\nabla n(\boldsymbol{r})|^2}{n(\boldsymbol{r})}\, \mathrm{d}\boldsymbol{r} \\ &= -\frac{1}{4} \iint n^{1/2}(\boldsymbol{r})[\delta(\boldsymbol{r} - \boldsymbol{r}')\nabla^2 + \nabla^2\delta(\boldsymbol{r} - \boldsymbol{r}')]n^{1/2}(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'. \end{aligned} \tag{3}$$

Following the basic structure of these double integrals, we can express $T_{\mathrm{X}}[n(\boldsymbol{r})]$ as

$$T_{\mathrm{X}}^{\alpha,\beta}[n(\boldsymbol{r})] = \iint n^{\alpha}(\boldsymbol{r})w_{\alpha,\beta}(\boldsymbol{r}, \boldsymbol{r}')n^{\beta}(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}', \tag{4}$$

where the kernel $w_{\alpha,\beta}(\boldsymbol{r},\boldsymbol{r}')$, which in principle has quadratic scaling, is often approximated as $w_{\alpha,\beta}(k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|)$ to obtain linear scaling. This approximation removes the density dependence of the kernel, since only a reference density enters the equation. The parameters α and β are obtained by imposing recovery of the known limits from above as constraints.

Kinetic energy functionals with density-dependent (DD) kernels have been suggested previously [30], but these functionals are computationally expensive (scaling quadratically with grid size). Recently, a new functional was proposed [20] which makes the linear response kernel density dependent without losing the sought-after linear scaling (by virtue of a Taylor series expansion of the response kernel). This new functional has a $T_{\mathrm{X}}[n(\boldsymbol{r})]$ which is expressed as

$$T_{\mathrm{X}}^{\alpha,\beta,\gamma}[n(\boldsymbol{r})] = \iint n^{\alpha}(\boldsymbol{r}) w_{\alpha,\beta,\gamma}(\boldsymbol{r},\boldsymbol{r}') n^{\beta}(\boldsymbol{r}') \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}', \tag{5}$$

where the kernel is given by

$$w_{\alpha,\beta,\gamma}(\boldsymbol{r},\boldsymbol{r}') = w_{\alpha,\beta,\gamma}[\xi_{\gamma}(\boldsymbol{r},\boldsymbol{r}'), |\boldsymbol{r}-\boldsymbol{r}'|] \tag{6}$$

with

$$\xi_{\gamma}(\boldsymbol{r},\boldsymbol{r}') = \left(\frac{k_{\mathrm{F}}^{\gamma}(\boldsymbol{r}) + k_{\mathrm{F}}^{\gamma}(\boldsymbol{r}')}{2} \right)^{1/\gamma} \tag{7}$$

as the non-local, two-body Fermi wave-vector. Again, the parameters α, β, and γ are obtained from the constraints arising from imposing the known limits presented above. Unique, universal values of α and β are obtained, while the value of γ cannot be determined universally and must be regarded as the sole adjustable parameter of this functional.

It is possible to continue the development of kinetic energy density functionals by adding higher order response. Functionals containing quadratic response have been proposed [15,18], but we will not assess these functionals in this work. Preliminary investigations [20] showed that the linear response kinetic energy functional containing the DD-kernel yields both linear scaling and accuracy comparable to higher order response functionals.

In this paper, we have applied four kinetic energy density functionals containing density-independent (DI) kernels of the (4) type, and one functional containing a DD-kernel according to (5)–(7). All these functionals should produce the correct response behaviour, as well as satisfy, at least asymptotically, the limits (a) and (c) by construction. The Perrot [16] functional, with $\alpha = \beta = 1$, is not justified by any other arguments, while the Smargiassi–Madden (SM) [17] functional has $\alpha = \beta = \frac{1}{2}$ to satisfy condition (b). The Wang–Teter (WT) [15] functional, with $\alpha = \beta = \frac{5}{6}$, can be shown to represent (d) quite well, although not exactly [19]. The last of the functionals with DI-kernel is the Wang–Govind–Carter (WGC) [20] functional, which is constructed to be correct in the large q-limit, (d), which yields uniquely $\alpha, \beta = \frac{5}{6} \pm \sqrt{5}/6$. The functional with the DD-kernel is a generalization of the WGC functional, where α and β are not changed, and the additional parameter γ is used to add features of (b) to the functional [20].

3. Method

The DFT is exact, but the form of the exchange and correlation energy is unknown and needs to be approximated. In this work, we have used the local density approximation (LDA) [11] to evaluate the exchange and correlation energy in both the KS and OF implementations of DFT. For solids, the LDA yields bulk properties in good agreement with experiments, although it usually underestimates lattice parameters and overestimates bulk moduli slightly. The generalized gradient approximation (GGA) usually yields increased lattice parameters and decreased bulk moduli compared with the LDA, which will put the GGA results closer to

experimental values for, e.g. Al [31], but the LDA is performing well enough for the test of the kinetic energy functionals, which is the purpose this work. Also, there are more results published from KS-LDA calculations for the systems of interest, especially for the β''-phase [32].

The most important aspect of a pseudopotential is its transferability, i.e. how accurately the pseudopotential will give, for a variety of atomic configurations, the same valence electron density in the interatomic region in comparison with an equivalent all-electron calculation. In the KS-DFT scheme, it is possible to take advantage of the KS-orbitals to project out different angular momentum components of the all-electron potential, thereby increasing the degrees of freedom in, and accuracy of, the pseudopotential. These NLPPs are known to have good transferability, if properly constructed. In the OF-DFT scheme, there are no orbitals, and only LPPs can be used. The lower flexibility of these LPPs generally yields less transferability, and therefore it is crucial to test the LPPs against results from NLPP calculations.

To assess the quality of the LPPs and to obtain reference results for assessing the kinetic energy functionals, we first carry out traditional KS periodic DFT calculations with a plane-wave basis, using non-local, norm-conserving Troullier–Martins pseudopotentials [33] for Al ($r_{\text{cutoff},s} = 0.95\,\text{Å}$, $r_{\text{cutoff},p} = 1.06\,\text{Å}$, $r_{\text{cutoff},d} = 1.14\,\text{Å}$) and Mg ($r_{\text{cutoff},s} = 1.24\,\text{Å}$, $r_{\text{cutoff},p} = 1.70\,\text{Å}$, $r_{\text{cutoff},d} = 1.66\,\text{Å}$). The kinetic energy cutoff for the plane-wave basis used to achieve convergence (to within $1\,\text{eV atom}^{-1}$) in the total energy was $500\,\text{eV}$ for both elements when NLPP were used.

The LPP for Al [23] we employed has been used extensively before. In the LPP KS-LDA calculations, the converged kinetic energy cutoff was $350\,\text{eV}$. For Mg, the LPP was derived from first-principles OF-DFT calculations with a quadratic kinetic energy density functional [24]. This pseudopotential was used in all OF calculations in this work, and the kinetic energy cutoff required for convergence was $500\,\text{eV}$. For the β'' phase (Al$_3$Mg), a kinetic energy cutoff of $500\,\text{eV}$ was used.

Calculations for fcc Al utilized a cubic cell of four atoms, and a $12 \times 12 \times 12$ k-point grid in the KS-LDA calculations. For Mg, the hcp structure was run in the two-atom primitive cell with $14 \times 14 \times 8$ k-points, while the bcc structure employed the two-atom basic cubic cell with $10 \times 10 \times 10$ k-points. For β'', the cell was the four atom cubic fcc cell with the Mg atom in the corner and the Al atoms on the faces in accordance with the L1$_2$ structure, and we used at least $10 \times 10 \times 10$ k-points in the KS-LDA calculations. In each case, the k-point grid was large enough to achieve convergence of the total energy (to within $10\,\text{meV atom}^{-1}$).

The OF-DFT code [34] uses plane-waves to expand the electron density. The expansion of the electron density usually converges for kinetic energy cutoffs 2–4 times the KS-DFT cutoff energies for the same pseudopotentials. For the OF-DFT calculations, we have used $1225\,\text{eV}$ (=90 Ry) for Al, and $1633\,\text{eV}$ (=120 Ry) for both Mg and β'' (Al$_3$Mg). The minimization was done with the conjugate gradient algorithm for the DI-kernel functionals and the steepest decent algorithm for the DD-kernel functional, using the variational parameter $\sqrt{n(\boldsymbol{r})}$, as proposed in [34], from an initial guess of a uniform electron density.

4. Results

We calculated the lattice parameters, and bulk moduli for fcc Al, hcp and bcc Mg, and the β'' phase (Al$_3$Mg), as well as the formation energies of the bcc Mg and β'' phases. Calculations with KS-LDA and NLPPs gave benchmark results of the accuracy of DFT-LDA for these systems. These benchmarks were then used to assess the reliability of the LPPs through KS-LDA calculations with these pseudopotentials. Finally, we tested the kinetic energy

Table 1. The lattice parameter, a, bulk modulus, B, and total energy, E_{tot}, for fcc aluminium.

Method	a (Å)	B (GPa)	E_{tot} (eV atom^{-1})
KS, NLPP	3.96	83.6	−57.1940
KS, LPP	4.03	68.9	−58.3321
OF, $\alpha = \beta = 1$ (Perrot) [16]	4.06	71.0	−58.2999
OF, $\alpha = \beta = \frac{1}{2}$ (SM) [17]	3.96	69.8	−58.4403
OF, $\alpha = \beta = \frac{5}{6}$ (WT) [15]	4.04	72.3	−58.3303
OF, $\alpha = (5 + \sqrt{5})/6$, $\beta = (5 - \sqrt{5})/6$ (WGC) [20]	4.03	72.0	−58.3340
OF, n-dependent, $\gamma = 2.7$ (WGC) [20]	4.04	81.9	−58.3003
Other KS (all electron [31] and NLPP [32])	3.96–3.98	83–85	−57.2393
Experiment (RT) [39]	4.05	72.2	

Table 2. Lattice parameters, a and c, c/a ratio, bulk modulus, B, and total energy, E_{tot}, for hcp magnesium.

Method	a (Å)	c (Å)	c/a	B (GPa)	E_{tot} (eV atom^{-1})
KS, NLPP	3.11	5.08	1.630	36.9	−24.4782
KS, LPP	3.14	5.19	1.652	35.9	−24.3897
OF, $\alpha = \beta = 1$ (Perrot) [16]	3.18	5.21	1.640	33.2	−24.3453
OF, $\alpha = \beta = \frac{1}{2}$ (SM) [17]	3.08	5.01	1.628	36.7	−24.5031
OF, $\alpha = \beta = \frac{5}{6}$ (WT) [15]	3.16	5.17	1.637	34.9	−24.3757
OF, $\alpha = (5 + \sqrt{5})/6$, $\beta = (5 - \sqrt{5})/6$ (WGC) [20]	3.16	5.17	1.636	34.9	−24.3804
OF, n-dependent, $\gamma = 2.7$ (WGC) [20]	3.17	5.17	1.634	42.0	−24.3690
Other KS, NLPP [32, 35–38]	3.09–3.18	5.01–5.16	1.61–1.63	37–40	−24.6085
Experiment (RT) [39]	3.21	5.21	1.623	35.4	

density functionals through OF-LDA calculations, using the results from the LPP–KS-LDA calculations as benchmarks.

The results of NLPP–KS-LDA calculations (tables 1–4) were compared with published KS-LDA results (all-electron [31] and NLPP [32, 35–38] calculations) as well as experiments [39–41]. The total energies are provided in the tables in order to allow quantitative comparison of the approximations to the non-interacting KS kinetic energy, when the same LPPs are employed in both KS and OF-DFT calculations. The bulk moduli were evaluated using the Murnaghan equation of state [42] with data points within ±5% of the equilibrium value. The agreement with other calculations is excellent, while the comparison with experiments shows the well known characteristics of the LDA: underestimated lattice parameters and overestimated bulk moduli. (Generally, errors in the bulk moduli of around 10% are very common.) The switch to LPPs in the KS-LDA calculations shows that these latter pseudopotentials are doing well. Comparing to the NLPP–KS-LDA benchmarks, the lattice parameters are somewhat larger and the bulk moduli somewhat lower, which brings the results for the LPPs, fortuitously, closer to experimental values. This is expected, since the single adjustable parameter of the empirical Al LPP [23] is fitted to the experimental lattice parameter, and the *ab initio* Mg LPP was constructed from KS-DFT bulk densities for which the lattice parameter was fixed at the experimental value [24]. The results from KS-LDA calculations with LPPs were then used as the benchmarks for the OF-LDA calculations.

Table 3. Lattice parameter, a, bulk modulus, B, total energy, E_{tot}, and formation energy, $\Delta H = E_{bcc} - E_{hcp}$ for bcc magnesium. The experimental result is an extrapolated, thermodynamically-based estimate.

Method	a (Å)	B (GPa)	E_{tot} (eV/atom)	ΔH (meV/atom)
KS, NLPP	3.49	37.8	−24.4481	30
KS, LPP	3.54	35.2	−24.3542	35
OF, $\alpha = \beta = 1$ (Perrot) [16]	3.58	33.0	−24.3142	31
OF, $\alpha = \beta = \frac{1}{2}$ (SM) [17]	3.46	36.0	−24.4667	36
OF, $\alpha = \beta = \frac{5}{6}$ (WT) [15]	3.56	33.5	−24.3433	32
OF, $\alpha = (5 + \sqrt{5})/6$, $\beta = (5 - \sqrt{5})/6$ (WGC) [20]	3.55	33.4	−24.3451	33
OF, n-dependent, $\gamma = 2.7$ (WGC) [20]	3.55	31.8	−24.3442	25
Other KS, NLPP [36, 35]	3.48–3.54	35–39		30–40
Experiment ($T = 0$) [40]				48

Table 4. Lattice parameter, a, bulk modulus, B, total energy, E_{tot}, and formation energy, $\Delta H = E_{tot}^{\beta''} - (3 * E_{tot}^{Al} + E_{tot}^{hcp\ Mg})/4$ for the β'' phase. The experimental lattice parameter is an estimate from the assumed linear relation between Mg concentration and lattice parameter for a dilute Al–Mg alloy [41]. The experimental results for ΔH are derived from the results of [2, 3, 7].

Method	a (Å)	B (GPa)	E_{tot} (eV atom^{-1})	ΔH (meV atom^{-1})
KS, NLPP	4.05	70.6	−49.0228	−8
KS, LPP	4.12	56.4	−49.8509	−4
OF, $\alpha = \beta = 1$ (Perrot) [16]	4.19	47.5	−49.7759	+35
OF, $\alpha = \beta = \frac{5}{6}$ (WT) [15]	4.15	53.7	−49.8003	+41
OF, $\alpha = (5 + \sqrt{5})/6$, $\beta = (5 - \sqrt{5})/6$ (WGC) [20]	4.15	53.0	−49.8047	+41
OF, n-dependent, $\gamma = 2.7$ (WGC) [20]	4.10	64.5	−49.8218	−4
Other KS, NLPP [32]	4.04			−15
Experiment (RT)	4.15			−12 to −16

First, the kinetic energy density functionals were tested on the properties of fcc aluminium. Since Al has a nearly-free-electron-like density, we expect that all linear response kinetic energy functionals should do well. The results for fcc Al are shown in table 1, and they agree well with the previously reported results [19, 20]. Three of five kinetic energy functionals reproduce extremely well the bulk properties of pure Al: the WT, WGC DI-kernel and the WGC DD-kernel functionals. Of the other two, the Perrot functional is doing surprisingly well, while the SM functional is giving acceptable results.

The electron density of Mg is less free-electron-like than that of Al, which presents a more difficult task to the kinetic energy density functionals [43]. For Mg, we have calculated the properties of both the ground-state hcp structure and the bcc structure. For the hcp structure (table 2), the WT and WGC DI-kernel functionals give the best results compared to LPP–KS-LDA and the WGC DD-kernel functional is also doing well. The Perrot functional is doing fairly well, while the SM functional is giving the worst results again (note especially the deviation in the c lattice parameter). For the bcc structure (table 3), the lattice parameter and bulk modulus results are similar with the WT and WGC DI-kernel functionals, together with the WGC DD-kernel functional giving good results. The Perrot and SM functionals

are performing a bit less well. The formation energy, ΔH, for the phase transition between the hcp and bcc structures of Mg is more sensitive to the accuracy of the models than the lattice parameters and bulk moduli. The OF calculations yields formation energies that are within the accuracy of the calculations, although the WGC DD-kernel yields a ΔH that is on the verge of being too low.

Finally, we performed OF calculations for the β'' phase (Al$_3$Mg). This is an even greater challenge for the kinetic energy density functionals, since the electron density in a mixed system is even further away from the nearly-free-electron gas. The results for the β'' phase are shown in table 4. The SM functional has convergence problems for the mixed Al–Mg systems, therefore we present no results for this functional for β''. The results for the lattice parameter and bulk modulus show similar trends as for the pure element phases: the WT, WGC DI-kernel and WGC DD-kernel functionals yield results consistent with the KS benchmarks, while the Perrot functional is doing less well. It is the formation energy, ΔH, that provides the main test of the kinetic energy density functionals. Since β'' is a meta-stable phase, it should have ΔH slightly negative, consistent with the KS results and experimental estimates. None of the DI-kernel functionals are able to give even simply a qualitatively correct ΔH. It is only the WGC DD-kernel functional that yields $\Delta H < 0$. Also, this result is in excellent agreement with the KS-LDA result with the LPP. The density dependence in the response kernel is crucial to give a qualitatively correct formation energy for the mixed Al–Mg system.

To summarize, the well justified WT and WGC DI-kernel functionals are doing well for lattice parameters and bulk moduli for all systems, as well as the formation energy for the bcc-phase of Mg, but the formation energy, ΔH, of the β'' phase (Al$_3$Mg) is qualitatively incorrect. To obtain ΔH correctly, the functional must include a DD response kernel which will be more sensitive to the variations in the density. The Perrot functional, whose exponents in the $T_X[n]$ term of (4) are not well justified, is doing surprisingly well. On the other hand, the SM functional, whose exponents are von Weizsäcker-like, has an unexpectedly poor performance in this test.

5. Discussion

The kinetic energy functionals we have utilized in this work are designed to recover linear response behaviour. The least justified functional, the Perrot functional ($\alpha = \beta = 1$), is doing surprisingly well for all systems examined.

The other functionals used here have been constructed by taking the properties of different limits into account. The SM functional ($\alpha = \beta = \frac{1}{2}$) has been constructed to fulfill the CGE up to second order. Although, the SM functional is more justified than the Perrot functional, it is not doing as well. One plausible cause might be that the SM functional gives a poor representation of the Lindhard response functional for a rapidly varying density, i.e. in the large q-limit [19].

The WT functional ($\alpha = \beta = \frac{5}{6}$) gives a better representation in the large q-limit [19] compared to the SM functional. The WGC functional ($\alpha = \beta = \frac{5}{6} \pm \sqrt{5}/6$) is constructed to give the correct large q-limit [20]. The results from these two functionals are very good for the pure elements, indicating that the large q-limit has to be taken into account when a kinetic energy functional is constructed. Also, these functionals give more or less identical results.

None of the four functionals above have a DD response kernel, and none of them are able to give a qualitatively correct formation energy for the β'' phase. It is only the functional with a DD-kernel [20] that gives a qualitatively correct result for the formation energy. The DD-kernel improves the performance of the functional for systems with large changes

in the electron density. Previously reported results [20] for vacancies and surfaces show that the DD-kernel functional give excellent results for the vacancy formation energy, and good results for the (111), (100), and (110) surfaces energies for Al, while the DI-kernel functionals fail in many respects. Also, when the electron densities were compared to the KS densities for the surfaces, the DD-kernel functional densities showed a not unimportant improved agreement over the DI-kernel functional densities. Apparently, alloys introduce large enough variations in the electron density to make the performance of the DI response kernel functionals poor.

The formation enthalpy of the β'' phase was calculated with both traditional KS-DFT and the OF-DFT. For the kinetic energy functional with a DD-kernel, the formation energy for OF-DFT is close to the one obtained from KS-DFT. To assess these formation energies, we have analysed the data from calorimetric measurements on Al–Mg alloys [2, 3, 6]. Although the measurements from Osamura and Ogura [2] are believed to be the GP zone dissolution, their results give a reasonable estimate of the formation energies of the β'' phase. For a complete separation of Al-25 at% Mg alloy, the composition that our calculations simulate, our analysis yields a formation energy of $-12\,\mathrm{eV}\,\mathrm{atom}^{-1}$. The result from van Rooyen and co-workers [3] gives a formation energy of $-14\,\mathrm{meV}$. We have also extrapolated data from Starink and Zahra [6], which is said to be due to the combined effect of GP zones and β''. For these data, we obtain a formation energy of $-16\,\mathrm{meV}\,\mathrm{atom}^{-1}$ to compare with our calculated data. Note that the experimental data for the β'' phase are acquired at temperatures slightly above room temperature while the calculated data correspond to $T = 0\,\mathrm{K}$. However, the approximations used in evaluating the experimental data are probably the main source of errors in our estimates of the formation energy, and these errors are likely to be larger than those due to the temperature difference. The OF prediction, using the WGC DD-kernel functional, of the formation energy of β'' is in qualitative agreement with both experimental estimates and agrees exactly with the KS-LDA prediction using the same pseudopotentials. This suggests that the OF-DFT, with LPPs and the DD-kernel functional, is doing as well as traditional KS-DFT, with the same LPPs, for Al–Mg alloys.

6. Conclusions

We performed calculations to assess the possibility to use an OF implementation of the DFT to calculate properties of Al–Mg alloys. The lattice parameter, bulk modulus, and formation energy of the meta-stable phase β'' have been calculated for five kinetic energy functionals which include correct linear response behaviour. One of these functionals has a DD response kernel, making it more sensitive to changes in the electron density. We find that it is only the functional with a DD-kernel that gives a physically reasonable formation energy for β'', in good agreement with both KS-DFT predictions and experimental estimates.

Our results show that OF-DFT with the DD-kernel kinetic energy density functional works well for Al–Mg alloys, and that the LPPs are of roughly the same quality as the non-local ones. Ongoing work is extending OF-DFT to non-metals, e.g. Si [44]. This conclusion opens up new possibilities to analyse properties of Al–Mg, and even Al–Mg–Si, systems of unprecedented size and complexity in the near future.

Acknowledgments

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