On the stability of random and intermetallic phases of LiAl alloys

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Abstract. We investigate the structural stability of the various random and intermetallic phases observed in the experimental phase diagrams of the LiAl system. A second-order pseudopotential theory is used in conjunction with the virtual crystal approximation to describe the structural energies of the random substitutional alloys. On the other hand we employ the augmented-spherical-wave (ASW) method on the same footing to calculate the total energies for the corresponding ordered phases. Even though these two methods are based on entirely different approaches, it is interesting to examine their separate roles in explaining the relative stability of different phases of LiAl alloys.

1. Introduction

Owing to their technological importance the investigation of the LiAl alloys has drawn much attraction. Looking at the phase diagram [1] of this system it is noticed that under the solidus various crystalline phases are stable at various ranges of concentrations and temperatures. Some of these phases are substitutionally disordered with simple underlying lattices, while some are stable with complex intermetallic structures; the latter are usually formed at stoichiometric compositions. The Li-rich alloys have a greater tendency to form these complex structures than Al-rich alloys. Around 50–50 composition the stable disordered BCC phase, over a broad range of temperatures, appears as a boundary separating the two regions of alloy concentration. In the limit of low temperature there is a predicted $\beta \Longleftrightarrow \beta'$ order–disorder phase transformation [1] occurring at this concentration. It is relevant to mention here that even though the technologically important range of concentrations lies between Al-rich and the 1–1 stoichiometry, in the present investigation we emphasize the ordered and disordered alloys stable over the entire range of concentrations of Li–Al alloys.

In the present calculations we have primarily employed the pseudopotential theory [2] to testify the stability of the disordered alloy phases stable at various ranges of concentration. This in particular enables us to examine the $\alpha(\mathrm{FCC}) \Longleftrightarrow \beta(\mathrm{BCC})$ phase transformation observed in the LiAl system. In this respect we stress the effect of the celebrated electron-per-atom ratio [3] stabilizing a particular structure over

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other probable structures. This is essentially related to the so-called Brillouin zone–Fermi surface (BZ–FS) interaction [4] recently established on firm basis [5, 6] for the Hume–Rothery types of alloys. The relevant formulation is based on a second-order perturbation theory suitable for simple metallic alloys like the Li–Al system.

Now, in principle, the pseudopotential theory may be employed to calculate the energies of ordered phases [7] as well, but that involves a number of order parameters [8] apart from those from the pseudopotentials themselves. In addition, these order parameters enter the theory as disposable parameters and thus a great degree of uncertainty always remains in that type of calculation. Apart from that, the inherent nucleation relevant to any such ordering in the atomistic range is not well understood in such a pseudoatom approach, particularly in terms of the virtual-crystal approximation [9]. Thus we need an *ab initio* approach to investigate the structural stability of the ordered intermetallic compounds observed in the LiAl alloys at various stoichiometries.

Recently Sluiter *et al* [10] investigated the phase equilibria in the LiAl system by calculating the total energies of the FCC and BCC based intermetallic compounds. They have employed the full-potential linearized-augmented-plane-wave (FLAPW) method to calculate the total energies; the latter have been correlated with the Connolly–Williams [11] prescription to obtain the many-body cluster interactions. The cluster interactions have been introduced in a statistical model called the cluster variation method (CVM) for calculating the configurational free energies complemented with other empirical contributions. Recently Guo *et al* [12] advanced similar calculations for the so-called *interloper* phases relevant to the LiAl system. Now the FLAPW method is certainly more refined than the augmented-spherical-wave (ASW) method for certain specific reasons; we also believe that for static lattices the inherent physics will not drastically depend on the choice of either method. This is simply because the basic concept of the linear-density approximation remains completely unaltered. The full-potential approximation, however, generates more refined values of the band energies and hence of the transport and optical properties; but, so far as the global energies are concerned, the ASW method is as good as the FLAPW—this is expected because the Fermi energies are reproduced quite identically by both the methods. In addition, computationally the ASW method is more economic. Owing to these attractive features, in the present investigation we have employed the augmented-spherical-wave (ASW) method [13] to calculate the total energies for the FCC and BCC based intermetallics. This method involves no adjustable or experimentally determined parameters; the only approximations involved are that the lattice consists of spherical atoms compressed into finite volume appropriate to a typical solid, and the adoption of the local-density approximation [14]. The relevant interatomic interactions enter the theory through the spatial distribution of the electrons in the appropriate states; in this respect boundary conditions that allow the atomic valence levels to have finite width are adopted in an appropriate way. The ASW is essentially a direct descendent of the linear muffin-tin-orbital (LMTO) [15] method and for pure systems it resembles the Korringa–Kohn–Rostoker (KKR) method [16]. These points imply the suitability of this method for calculating the total energies of the elemental and alloy systems to a higher degree of accuracy.

The layout of the paper is as follows: in section 2 we briefly describe the pseudopotential formalism appropriate to a disordered binary alloy. In section 3 we describe the essence of the ASW method. Results for the two approaches are presented and discussed in section 4. Finally, we make some concluding remarks in section 5.

2. Total structural energy: pseudopotential approach

We consider a static binary alloy $A_c B_{1-c}$ consisting of cN ions of valency Z_A and $(1-c)N$ ions of valency Z_B all contained in a volume Ω. Following Evans *et al* [5] the structural part of the configurational free energy of the alloy in the $T = 0$ K limit is written as†

$$F_S = \frac{1}{2\Omega} \sum_{q \neq 0} \chi(q)|\bar{v}(q)|^2 |S(q)|^2 \delta_{q,g} + \frac{1}{2\Omega} \sum_{q \neq 0} \frac{8\pi \bar{Z}}{q^2} (|S(q)|^2 - N)\delta_{q,g} \qquad (1)$$

where the first term is the effective band structure contribution describing the electron–ion interaction in a virtual-crystal approximation and the second term describes the ion–ion interaction; the latter is taken to be purely coulombic. The alloy pseudopotential $\bar{v}(q)$ and valency $\bar{Z}$ are given by $\bar{v}(q) = cv_A(q) + (1-c)v_B(q)$ and $\bar{Z} = cZ_A + (1-c)Z_B$ respectively, where A and B refer to the elemental components. The effective structure factor $S(q)$ corresponds to the underlying lattice. The interacting response function $\chi(q)$ is related to the non-interacting response function $\chi_0(q)$ via the effective electron–electron interaction potential $G_{ee}(q)$ as follows:

$$\chi(q) = \chi_0(q)[1 - G_{ee}(q)\chi_0(q)]^{-1} \qquad (2)$$

where $G_{ee}(q)$ is given by

$$G_{ee}(q) = 8\pi \bar{Z}/q^2 + G_{xc}(q) \qquad (3)$$

The exchange and correlation function $G_{xc}(q)$ in the present case is represented by the Ichimaru–Utsumi [17] local field factor.

Now using equation (2) in (1) we write

$$F_S = \frac{1}{2\Omega} \sum_{q \neq 0} \chi_0(q)|\bar{v}_{sc}(q)|^2 |S(q)|^2 \delta_{q,g} - \frac{1}{2\Omega} \sum_{q \neq 0} \chi_0^2(q)|\bar{v}_{sc}(q)|^2 U_{ee}(q)|S(q)|^2 \delta_{q,g}$$

$$+ \frac{1}{2\Omega} \sum_{q \neq 0} \left[\frac{8\pi \bar{Z}}{q^2} \right] (|S(q)^2| - N)\delta_{q,g} \qquad (4)$$

where in segregating the effective band structure contribution, we have used the prescription relating the interacting and non-interacting response functions with the bare (v) and screened pseudopotentials (v_{sc}) respectively (for details see Evans *et al* [5]). In equation (4) the first term is essentially an effective one-electron contribution to the free energy; this term describes the band structure of the neutral pseudoatoms. The second term corrects for double-counting of the electron–electron interaction which occurs in the first term; this term also takes care of the many-body effects via $G_{ee}(q)$. We call this term an extra band structure contribution to the free energy. Combining the second and third terms we obtain an effective neutral-object contribution that carries very little information about the structure of any crystalline phase [5]. However, in all calculations we consider all the terms to determine the structural phase stability.

† We use atomic units so that all energies are in rydbergs.

3. Total energy: ASW approach

In the last section we have briefly described the pseudopotential formulation and in this section we shall describe only the essence of the ASW method. The total energy per unit cell within the local density approximation is given by [13]

$$E_{\text{tot}} = \sum_i \epsilon_i - \frac{1}{2} \int_{\Omega_c} \rho(r) V_c(r) \, \mathrm{d}r - \int_{\Omega_c} [V_{\text{xc}}(r) - \epsilon_{\text{xc}}(r)] \, \mathrm{d}r - \frac{1}{2} \sum_\nu Z_\nu V_M(r_\nu) \quad (5)$$

where ϵ_i are the eigenvalues of the occupied states i obtained by solving the Kohn–Sham equation, Z_ν and $\rho(r)$ are the nuclear and electron charge densities respectively while $V_c(r)$, $V_{\text{xc}}(r)$ and $V_M(r)$ are respectively the Coulomb, exchange-correlation and Madelung potentials, and ϵ_{xc} is the exchange and correlation energy. For elemental systems for which the electronic and nuclear charges comprised in the unit cell cancel each other the relevant Madelung contribution becomes zero. Here we should make a note of the precaution that the Madelung energy defined in the pseudopotential perspective is a different entity in which this term is assumed to be the difference in electrostatic energy between a lattice of point ions and a uniform positive charge background.

We should mention here that all contributions to the total energy, other than the Madelung energy, are obtained from the independent compressed-atom calculations. The relevant conceptual constraints that define the environment of the compressed atoms are obtained self-consistently in terms of the ASW.

4. Total energy calculations

It is reiterated here that the pseudopotential theory defines the total energy on an entirely different basis from that of any *ab initio* method. The most striking difference arises from the concept that all pseudopotentials are weak and the so-called core cancellation theorem [18] is an essence of these pseudo electron–ion interactions, whereas, in any *ab initio* method, the valence electrons see the full potential and the core states are properly taken into account in any energy calculations. Nevertheless the cohesive energies, depending on their definitions, are expected to inherit some similarities in both the pseudopotential and *ab initio* methods.

In 4.1 we present and discuss in some detail results for the disordered phases of the LiAl system calculated in terms of the pseudopotential method. Results obtained from the *ab initio* ASW method on the intermetallic compounds will be presented in 4.2.

4.1. Structural energies and phase stability of disordered LiAl alloys: pseudopotential results

In the calculations we have used the Ashcroft empty-core pseudopotential with core radii of values 1.06 and 1.12 au assigned respectively to pure lithium and aluminium while their atomic volumes [18] are taken to be 144.9 and 111.3 au respectively. The computations engage an appropriate number of generated lattice vectors sufficient for proper convergence of the total structural energies. All calculations consider the Ichimaru–Utsumi [17] local field factor while the virtual-crystal approximation and Vegard's rule are adopted throughout; we present detailed discussions explaining the

validity of these approximations in the concluding section. The empty-core radii are assumed to be transferable from elemental states to the alloy phases.

Results for energy differences between the FCC and BCC structures for the LiAl system are presented in figure 1. From figure 1(*a*) we notice that the one-electron band structure contribution entirely dominates the structural prediction while the neutral-object contribution does not show any remarkable feature as a function of concentration.

The striking aspects of the energy difference curves are that they exhibit a symmetric variation of the stable crystal structures with the sequence BCC–FCC–BCC–FCC with the transitions at the approximate electron-per-atom ratio of 1.10, 1.40, 2.02 respectively. These are indeed the values at which the first FCC, first BCC and the second FCC reciprocal lattice vectors are about to cross the respective Fermi surfaces. This is the essence of the so-called Brillouin zone–Fermi surface (BZ–FS) interaction lying at the heart of phase stability of the Hume-Rothery alloys [5]. The present calculations show the FCC phase to be stable over the BCC phase along the entire Al-rich concentrations; the BCC phase starts to stabilize at around 50–50 concentration and it remains stable over a wide range of concentrations. This observation in particular supports the stability of the disordered β phase observed at 50–50 concentration in the phase diagram.

Now we would like to discuss the roles of the many-body effects on the stability of the disordered alloy phases. In this respect we have noted (see figure 1(*b*)) that replacing the Ichimaru–Utsumi [17] exchange and correlation function by the Sham–Hubbard [19] function does not noticeably affect either the energy differences or the structural prediction. It is of course true that the excess thermodynamic quantities e.g. the internal energy of formation and so the cohesive energies are quite sensitive to the choice of the exchange–correlation functions [20]. However, any change in the values of empty-core radii r_c in the potential can noticeably change the magnitudes of the energy differences; but figure 1(*c*) shows that these changes hardly alter any structural prediction of the alloy system. These observations reveal that it is the logarithmic singularity associated with the non-interacting response function, and not the pseudopotential details, that decides the structural prediction of the disordered LiAl alloys.

As far as the elemental systems are concerned Al is clearly predicted to be FCC while for Li the structural prediction is less certain; for the latter the energy difference between the FCC and BCC structures is too small to predict the stable structure. Recent neutron diffraction measurements [21] show that Li undergoes a martensitic transformation from BCC to a hexagonal close-packed (HCP) structure at around 78 K. During the cooling process Li exhibits a stable FCC structure at around 100 K before the next stable 9R structure. We will make additional comments on these aspects at the end of 4.2.

4.2. Structural energies and phase stability of ordered intermetallics: ASW results

We have already mentioned that the ASW method is essentially an *ab initio* method aiming to calculate the electronic properties of ordered systems in terms of the independent compressed-atom model. The input data are the atomic number Z, the lattice parameters of the underlying lattice and the number of $\bar{k}$-points assigned to the reduced Brillouin zone; the distribution of the electronic charges among the various states is properly achieved self-consistently. We should reiterate here that to explain the results on the same footing, we have used the linearized values of the
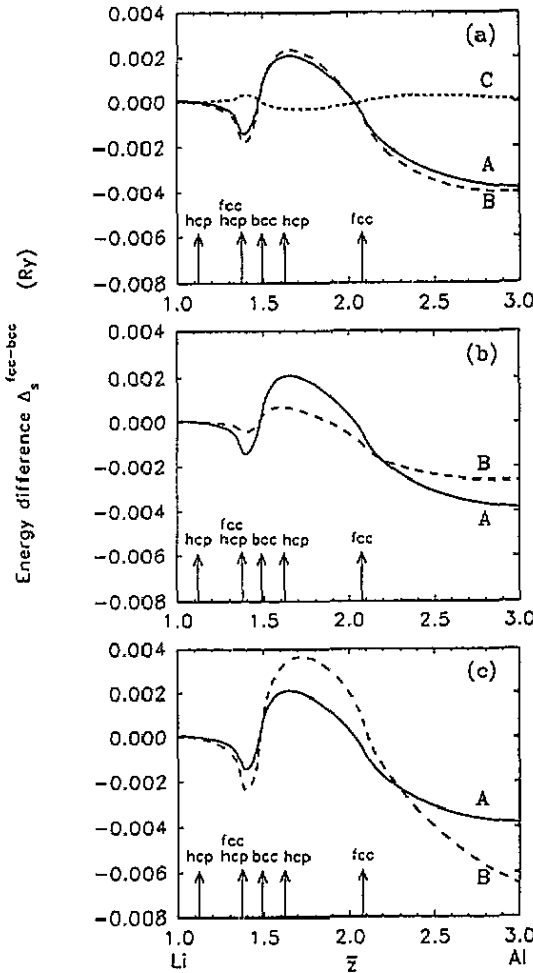
Figure 1. Pseudopotential energy differences per electron $F_S^{FCC} - F_S^{BCC}$ for LiAl as a function of the electron-per-atom ratio $\bar{Z}$. The arrows denote the electron-per-atom ratio in which various reciprocal lattice vectors cross $2k_F$. (a) Calculations use the Ashcroft empty-core pseudopotential with $r_c^{Li} = 1.06$ au and $r_c^{Al} = 1.12$ au and the Ichimaru–Utsumi exchange–correlation function. Curve A denotes the total energy differences $F_S^{FCC} - F_S^{BCC}$, curve B the differences in the one-electron energies and, curve C the differences in the neutral-object energies. (b) Curve A denotes the differences in total energies using the Ichimaru–Utsumi exchange and correlation function while curve B denotes those using the Sham–Hubbard exchange and correlation. (c) Curve A denotes the differences in total energies using $r_c^{Li} = 1.06$ au and $r_c^{Al} = 1.12$ au while curve B denotes those using $r_c^{Li} = 1.166$ au and $r_c^{Al} = 1.232$ au (10% increase). These calculations use the Ichimaru–Utsumi exchange and correlation functions.
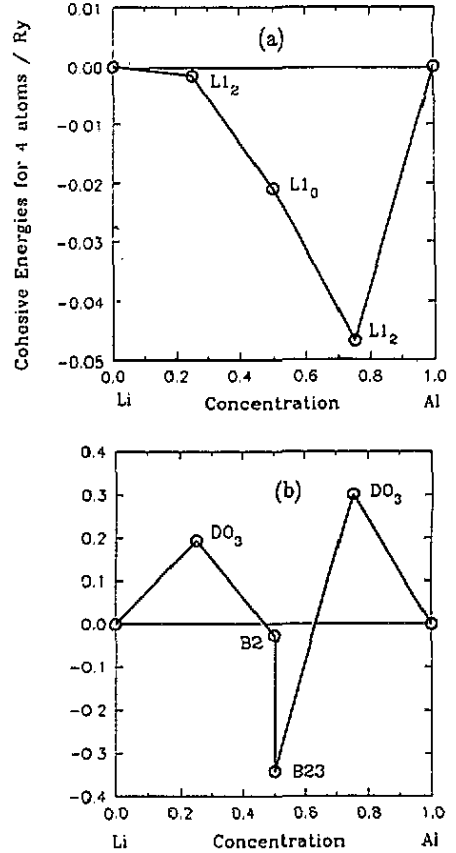
Figure 2. Cohesive energies per four atoms for the elemental and intermetallic compounds of LiAl as calculated by the ASW method. (a) Cohesive energies for the FCC-based compounds with $L1_2$ and $L1_0$ structures at various stoichiometries are denoted by circles; the lines connecting the circles are artificial. (b) Cohesive energies for the BCC-based compounds with DO_3, B2 and B23 structures at various stoichiometries; other details follow those of figure 2(a).

atomic volumes in both the pseudopotential and ASW calculations; relevant remarks are made on this aspect in the concluding section. Now the total energy calculated for any structure combines the sums of the kinetic energies of the core and valence states, sums of the eigenvalues of the core and valence states, the effective potential at the nucleus as seen by the electrons, the Hartree contribution, the many-body contributions and the contribution arising from the inherent pressure. All energies are essentially self-consistent.

We, in the first place, would like to look at the possibility of formation of the alloys by calculating the cohesive energies. Now there are two ways of defining the cohesive energies: one derives from the possibility of formation of the alloy from totally segregated atomic components and the other from the possibility of formation of the alloy from the solid components. In the present context we have looked at the latter possibility. In this case we have computed the cohesive energies in terms of the FCC- and BCC-based components. The results are presented in figure 2(a) and 2(b). Figure 2(a) shows that the FCC-based intermetallic compounds α_1: Li_3Al ($L1_2$), α_2: $LiAl(L1_0)$ and α_3: $LiAl_3(L1_2)$ may, in principle, be formed at the respective stoichiometries provided one starts with the elemental FCC Li and Al systems. Figure 2(b), in contrast, shows that the β_1: Li_3Al (DO_3) and β_2: $LiAl_3$ (DO_3) intermetallics may not be formed at all out of the solid BCC-based Li and Al systems; the β_3: $LiAl$ (B2) and β_4: $LiAl$ (B23) may be formed at 50–50 stoichiometry. The B23 structure, however, is largely favoured by the BCC-based components. Qualitatively our predictions compare very well with those obtained by the earlier calculations [10, 12, 22]. Here we should make a note of the fact that the definition of the cohesive energies varies in these calculations and so we have avoided any tabular comparison of the results.

To analyse the relative structural phase stability we have plotted the energy differences between the FCC- and BCC-based alloys in figure 3. The FCC-based $L1_2$ structure for both Li_3Al and $LiAl_3$ intermetallics is found to be stable over those formed out of the BCC-based DO_3 structure at the respective stoichiometries. At 50–50 composition the BCC-based B23 structure is found to be largely favoured over the FCC-based $L1_0$ structure. Looking back to figures 1(a)–(c) it is noticed that the pseudopotential calculations clearly predict a disordered BCC phase to be stable at around this concentration; the BZ–FS surface interaction confirms this stability. Thus the stability of a BCC-based ordered alloy—here the B23 phase—appears to be a natural consequence of this observation. The calculated density-of-states (DOS) at the respective Fermi levels for the B2 and B23 structures are found to be 3.96 and 6.12 states per Ryd cell, respectively. This reveals that the electronic part of entropy—which is directly related to the DOS at the Fermi level—for the B23 structure is much higher than that of the B2 structure; this feature on the contrary indicates that a larger electronic entropy, even in the ground state, will have a tendency to lower down the free energy implying a more stable structure. At this stage, however, it is not quite clear whether the appearance of the van Hove singularities in the DOS is playing any significant role in stabilizing the B23 structure against other relevant structures.

We may mention here that all energies are optimized with respect to the ratio of the atomic radii r_{Li} and r_{Al} at fixed lattice parameters. During this optimization procedure we note that in all stoichiometries the lithium atoms transfer a certain amount of charge to the aluminium atoms. Our calculations show that the Li atoms give away an amount of 0.09 and 0.24 au charges to the Al atoms relevant to B2 and
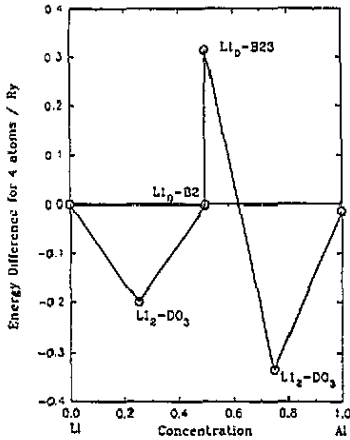
Figure 3. Differences in total energies E_{tot}^{FCC} − E_{tot}^{BCC} per four atoms for the elemental and intermetallic compounds of LiAl as calculated by the ASW method. The circles denote the energy differences between the FCC-based (L1$_2$, L1$_0$) and BCC-based (DO$_3$, B2, B23) intermetallics. The lines connecting the circles are artificial.

B23 structures respectively. This charge transfer may be viewed as a consequence of the covalent tendency of the Li atoms. This observation in general reveals the observed shrinking of the Li atom from its elemental size. The latter is found in all intermetallics of LiAl, but a large charge transfer may be partly responsible for the clear stability of the B23 phase over other intermetallics.

As far as the elemental systems are concerned, Al is clearly predicted to be FCC while Li opts equally for the BCC and FCC structures; the latter observation was also noticed in the pseudopotential calculations. Following this, we may conclude that the low temperature form of metallic lithium is essentially a combination of FCC, BCC and HCP lattices, as observed experimentally [21]. Calculations combining all these relevant structures are in progress.

5. Conclusions

In the present investigation we have examined the phase stability of the disordered and ordered phases of the LiAl system. For the disordered phases we have applied the second-order pseudopotential theory and for the ordered phases we have employed the ASW method. The two approaches have completely different bases; nevertheless, while applied on the same footing e.g. using the same number densities, we note some complementary observations regarding the stability of these phases. In the light of these observations we may make the following concluding remarks:

(i) First of all, the virtual crystal approximation (VCA) has been used in the pseudopotential calculations. It is, however, familiar that the VCA is applicable to systems with constituents having similar scattering properties. In the present case, apart from the size factor, the constituents Li and Al inherit some similar properties e.g. predominantly these are s–p bonded simple metals with very little ion-core polarizability; these features indicate that they are naturally weak scatterers. This observation leads to the conclusion that any probable Fermi-surface broadening will not substantially change the spherical topology of the Fermi surface indicating that the invoked BZ–FS interaction will not be seriously affected by any means. However, any finite-temperature calculation should include the relevant refinements properly.

We may mention here that any Korringa–Kohn–Rostoker (KKR)–coherent-potential-approximation (CPA) type of calculations [23] for the total energies may also be done on these systems; but the electronic structures of the components (Li and Al) reveal that the present perturbative calculations particularly looking for the structural energy differences should be as good as any KKR–CPA types of calculations. On the other hand the use of the VCA within the pseudopotential framework can effectively demonstrate the role of the BZ–FS interaction. Such a microscopic demonstration is not possible from any *ab initio* calculation.

(ii) Secondly, in all calculations we have assumed Vegard's rule for the lattice constant. However, a recent set of pseudopotential and KKR–ASW calculations by Masudo-Jindo and Terakura [24] show that the lattice constant of the Li–Al system varies non-monotonically as a function of concentration. This variation has been explained in terms of the first-order perturbation theory of the pseudopotentials. This phenomenon clearly reveals that these are essentially the volume terms and not the pairwise interactions that are affected by any non-Vegard trend of the lattice constant variation. On the contrary, this implies that the non-monotonic variation of the lattice constant has practically very little to do with the details of the band structures of any alloy, whether ordered or random. Consequently, any probable effect, if there be any, will not visibly affect the BZ–FS interaction invoked in the pseudopotential calculations. This explanation is also shared by the calculations of Masudo-Jindo and Terakura [24]. It is, of course, essential to check whether the calculated free-energy minima can generate similar values of the lattice constants.

(iii) A higher-order theory may prove to be more decisive; however, our experience [25] reveals that the higher-order terms in the free energy merely supplement the second-order theory in explaining the stability of random phases. The question regarding the transferability of pseudopotentials from elemental systems to the alloys still remains a drawback in the pseudopotential theory. Even though this is not a special obstacle in the present context, it may prove to be crucial for other purposes [26].

(iv) As far as the structural prediction is concerned, the present application of the ASW for calculating the total energies for the intermetallics of the LiAl system has been found to be quite in line with that of the full-potential linearized augmented-plane-wave (FLAPW) calculations by Sluiter *et al* [10]. Any finite-temperature thermodynamic calculation may make a more conceivable comparison. However, sensitive properties, such as formation energy, bulk modulus and elastic properties, which involve much smaller energy differences and in these cases a more precise method is certainly needed.

(v) Although the application of the pseudopotential theory and the ASW on the same footing has certain appealing features, this approach may be criticized on the point that the two methods are based on two different physical concepts. Regarding this point we should mention that the ASW may, in principle, be correlated with the (substitutionally) disordered alloys as well; but at the moment any CPA-like descendent of the ASW does not exist and any endeavour along this line may somewhat affect the prime theme of the ASW [27]. However, an attempt to develop a CPA-like descendent of the ASW could be interesting.

In view of some of the remarks made above it will be appropriate to correlate the ASW theory with finite-temperature properties via some tractable scheme; this will allow us to understand the dynamic aspects of nucleations that enhance the

formation of the various alloy phases discussed in this paper. We should however sound a note of caution here that correlation of the ground-state linear density functional theory with finite-temperature properties on the assumption that electrons are less hot than ions may not be appropriate for hot crystals. In addition any semi-empirical approximation for entropy and classical modelling of the liquid state may raise serious questions while attempts are made to reproduce phase diagrams. So an effort towards developing a global first-principles theory on a unified basis that will consider the temperature-dependent quantities in a self-consistent fashion would be the correct continuation of this work.

Acknowledgments

References

[1] Mondolfo L F 1976 *Aluminum Alloys* (London: Butterworth) pp 82, 308
[2] Rahman S M M 1979 *PhD Thesis* University of Bristol
[3] Hume-Rothery W 1932 *The Metallic State* (London: Oxford University Press) p 328
[4] Mott N F and Jones H 1936 *The Theory of the Properties of Metals and Alloys* (London: Oxford University Press) p 170
[5] Evans R, Lloyd P and Rahman S M M 1979 *J. Phys. F: Met. Phys.* **9** 1939
[6] Rahman S M M 1988 *Int. J. Phys.* **B2** 1
[7] Rahman S M M 1981 *J. Phys. F: Met. Phys.* **11** 1011
[8] Cowley J M 1950 *Phys. Rev.* B **77** 667; 1960 *Phys. Rev.* **120** 1648
[9] Evans R 1979 *Electrons in Disordered Metals and at Metallic Surfaces (NATO ASI Series, vol 42)* ed P Phariseau, B L Györffy and L Scheire (New York: Plenum) p 417
[10] Sluiter M, de Fontaine D, Guo X Q, Podloucky R and Freeman A J 1990 *Phys. Rev.* B **42** 10 460
[11] Connolly J W and Williams A R 1983 *Phys. Rev.* B **27** 5169
[12] Guo X Q, Podloucky R and Freeman A J 1990 *Phys. Rev.* B **42** 10 912
[13] Williams A R, Kübler J and Galatt C D Jr 1979 *Phys. Rev.* B **19** 6094
[14] Hedin L and Lundquist B I 1971 *J. Phys. C: Solid State Phys.* **4** 2064
[15] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[16] Korringa J 1947 *Physica* **13** 392
     Kohn W and Rostoker N 1954 *Phys. Rev.* **94** 111
[17] Ichimaru S and Utsumi K 1981 *Phys. Rev.* B **24** 7385
[18] Cohen M and Heine V 1970 *Solid State Physics* vol 24 (New York: Academic) p 196
[19] Sham L J 1965 *Proc. R. Soc.* A **283** 33
[20] Young W H 1986 private communication
[21] Smith H G 1987 *Phys. Rev. Lett.* **58** 1228
[22] Hafner J and Weber W 1986 *Phys. Rev.* B **33** 747
[23] Johnson D D, Nicholson D M, Pinski P J, Györfy B L and Stocks G M 1990 *Phys. Rev.* B **41** 9701
[24] Masudo-Jindo K and Terakura K 1989 *Phys. Rev.* B **39** 7509
[25] Rahman S M M and Rahman M M 1985 *J. Phys. F: Met. Phys.* **15** 447
[26] Rahman S M M, Hasegawa M, Hoshino K and Young W H 1987 *Phys. Chem. Liq.* **17** 21
[27] Kübler J 1992 private communication