Charge-transfer effects in disordered alloys: the test case of Al - Li alloys

Charge-transfer effects in disordered alloys: the test case of Al–Li alloys

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Abstract. A general method for treating the so-called charge-transfer effects in substitutional alloys is suggested within the formalism of the single-site (SS) coherent-potential approximation (CPA). The method allows the self-consistent treatment of the Poisson field through the construction of a configurational space and species-dependent structure constants which provide the means for an application of multiple-scattering theory which avoids overlap between adjacent cells. This, in turn, allows the treatment of non-neutral cells at the level of the SS CPA, avoiding the need for subsequent correction the results of the CPA. The method is compared with previous approaches to the problem and is used to treat the case of Al–Li alloys for which significant charge transfer is known to exist. The results are compared with those obtained within the muffin-tin implementation of the CPA, and a final discussion of the general features of the proposed method is given.

1. Introduction

The search for the electronic origins of phase stability and related properties of solid materials within the single-electron approximation is based on the solution of two interconnected equations, namely the Schrödinger equation and the Poisson equation. The solution of the Schrödinger equation for a given potential in which the electrons move results in the identification of the band structure of the material and allows the calculation of the so-called band energy part of the total ground-state energy of the system. The electrostatic interactions in the material and the self-consistent determination of the potential are directly related to the Poisson equation [1]. In modern calculations of the electronic structure of ordered solids, these two different equations can be treated within a single procedure to yield often very accurate results.

The consistent treatment of the Schrödinger equation and the Poisson equation is no longer straightforward in the presence of substitutional disorder in the system. Now, great inaccuracies can arise in the calculation of the electrostatic energy because of the possible replacement of the average of products of charge densities by the products of averages. Therefore, a great deal of effort has been expended [2–9] recently in attempts to provide a proper treatment of the electrostatics in substitutionally disordered alloys.

It is the purpose of this paper to show that there is a unique self-consistent treatment of charge-transfer effects in substitutionally disordered alloys based on the formal construction

discussed in the preceding paper. This method is based on the ideas embodied in the coherent-potential approximation (CPA) [10–18] as implemented within the formalism of Blackman, Esterling and Berk (BEB) for the treatment of alloys with diagonal as well as off-diagonal disorder [19, 20]. The original work by BEB was designed to treat differences in band width between the alloy constituents in their pure (unalloyed) states. Here, the same formal approach is used to treat the effects of non-neutral cells in a disordered substitutional alloy.

In contrast with previous approaches to the problem, the method introduced here can be shown to satisfy a number of desirable properties including the proper analytic structure of the electron self-energy and the simultaneous treatment of both the Schrödinger equation and the Poisson equation. It also leads to a proper alloy theory whose domain is not limited to the calculation of the total ground-state energy of an alloy but encompasses essentially all physical properties and makes unique predictions about properties related to the electronic structure of a system such as electronic transport and the study of phase stability and ordering trends in disordered systems. Furthermore, it allows the application of well established perturbative corrections to the CPA results, which in turn allow the study of statistical fluctuations in the local environment of a site and their effect on electronic structure, chemical order and stability.

2. Preliminary notions

In the discussion which follows, we shall assume that the calculation of the electronic structure is carried out within a full-cell treatment of both the Schrödinger equation and the Poisson equation, which means that we do not use the method of spherically averaging the cell potential and charge density in the development of the formalism. In carrying out numerical calculations, it is still necessary to employ such approximations and we shall discuss their effect in connection with the numerical results presented below. At the same time, much of the conceptual basis of the attempts to treat charge transfer can be illustrated if one puts aside the purely numerical consequences of approximations to the potential and the charge in a cell.

It is clear at the outset that, in a proper electronic structure calculation based on a full-cell approach, the particular partition of a system into cells is immaterial. For example, one should obtain identical results for the electrostatic interaction regardless of the scheme chosen to identify the cells associated with a given atomic species, and of the amount of charge in those cells. This is certainly the case in an ordered system where it is always possible to evaluate the electrostatic interactions by means of a Madelung summation technique. However, even in this case, it still seems to be profitable to partition the system in such a way that individual cells are charge neutral. This effectively reduces the calculation of the electrostatics of a system to a local region, leaving only the summation of higher multipole moments throughout the system which, at least for cubic materials, converge rapidly and are often numerically insignificant. This construction leads to equivolume cells in the case of monatomic systems but may lead to cells of different volumes for different species in systems containing atoms of more than one chemical species.

It would be meaningful also to use neutral cells in treatments in which cell potentials and charges are approximated by their spherical averages, as in the construction based on the atomic sphere approximation (ASA). In such treatments, which are indeed approximate compared with full-cell methods, all the electrostatic interaction can be confined within the spheres surrounding atoms of different species, provided that these spheres are individually neutral. However, in contrast with full-cell methods, calculations based on the ASA are

not independent of sphere sizes since variations in the sphere volume results in different approximate wavefunctions for the system. This circumstance can possibly be utilized to advantage through the treatment of sphere volume as a variational parameter. However, the size of the cell is *not* a proper variational parameter and such variational treatments may lead to unphysical effects such as a collapse of the volume of the system [21].

Reverting to a full-cell discussion, we turn to the case of disordered substitutional alloys. Now, the calculation of the electrostatics can become problematic if the Wigner–Seitz (WS) cells on a Bravais lattice, which by construction have equal volumes for all sites, are not found to be charge neutral. These difficulties arise primarily because of the lack of order which requires the performance of an average of the product of charges, or of charges and potentials. This must often be done through an approximation of the average of the product by the product of averages. If the cells were neutral, then the monopole terms would vanish identically and the procedure just described would have a small effect on calculated quantities (at least for cubic systems). In the case of charged cells, this procedure can lead to large inaccuracies in calculated quantities. The various attempts to treat charge-transfer effects in alloys reported thus far have concentrated largely on correcting for the errors produced by the replacement of the average of products by the product of averages.

In proceeding with our discussion, it is useful to keep in mind a number of basic ideas that come into play in the study of substitutionally disordered systems. First, even though the Schrödinger equation and the Poisson equation are interconnected in any calculation of the electronic structure, they define separate fields which must be treated independently. An approximation employed with respect to one of these fields does not necessarily provide an acceptable treatment of the other. This turns out to be the case in the application of the single-site (SS) CPA to treat the effects of chemical disorder on the scattering properties of an alloy. The SS CPA treats only the Schrödinger equation but provides no independent treatment of the electrostatics. However, the extent to which the cells used in the treatment of the scattering problem are charge neutral tends to minimize the effects of the lack of separate treatment of the Poisson equation.

Second, there exists no mean-field theory for treating the electrostatic interaction analogous to that of the CPA for the scattering problem. The infinite range of the Coulomb field precludes this approach, even when disorder induces a screening of 'net charges' that may be of very short range. Because of this, the notion of statistical charge fluctuation, as used in many treatments of alloy electrostatics, is not a well defined concept; there exists no underlying medium with respect to which fluctuations can be defined. Therefore, *one is required to provide a treatment of the full charge in the system, which is an observable, rather than charge fluctuations (which are not)*.

Third, *the results of calculations should be independent of the manner in which one chooses to define charge transfer*. It is constructive to keep in mind that charge transfer is defined with respect to a particular division of a material into cells and, consequently, is not uniquely determined by the charge itself. Therefore, in order to be a legitimate element of analysis, the concept of charge transfer should lead to results which are independent of its magnitude, or a particular partitioning of an alloy system into cells (as we mentioned above, an electronic structure calculation based on a full-cell treatment of the potential and charge would satisfy this requirement).

In addition, there are three subsidiary notions to be considered. First, any approximation introduced in treating disordered materials should be controlled in the sense that one can determine its effects in specific applications. Second, the results obtained in a particular calculation or any number of calculations, in and of themselves, do not suffice to prove the validity of a computational scheme at the formal level, regardless of their accuracy in

specific cases. Finally, it is highly desirable to produce not only a scheme for obtaining a valid estimate of the electrostatics of an alloy, but a *bona-fide* theory of disordered systems which provides a means for the study of a wide spectrum of properties related to the electronic structure.

3. Previous work

In discussing previous work to treat charge-transfer effects in alloys, it is convenient to classify the various attempts made according to the underlying methodology for calculating the electronic structure of alloys. In this regard, we can distinguish at least the following three categories:

(1) work based on the study of *ordered* alloys;

(2) work based on the explicit study of *disordered* alloys within the CPA, including non-perturbative corrections to the results obtained within the CPA;

(3) work based on perturbative corrections to the CPA.

3.1. Ordered alloys

In the most prevalent implementations [2, 3] of studying disordered systems through the study of ordered structures, the effects of charge transfer, or cell non-neutrality, are taken into account along the following lines.

(1) For each ordered structure studied, one partitions the material into equivolume WS cells and records the amount of electronic charge deficiency or excess compared with the nuclear charge as a function of the number of nearest neighbours of a specific kind in the vicinity of a site.

(2) The charge transfer is plotted as a function of near-neighbour environment (often resulting in a linear variation).

(3) Various forms depending on this charge transfer can then be used to obtain corrections to the electrostatic energy of an alloy.

One general expression suggested for evaluating these corrections in the case of binary alloys $A_{1-c}B_c$, where c is the concentration of the atoms of type B, takes the form

$$\Delta E = -\beta \, \mathrm{e}^2 c(1-c) \frac{(Q_A - Q_B)^2}{R_1} \tag{3.1}$$

where Q_A and Q_B are the net charges in cells of type A or B, and R_1 is the radius of the first coordination shell.

In using this expression, it is found that the value of β must be adjusted, essentially on a case-by-case basis, in order to give results that correspond to specific systems. In the summary of the application of this expression given by Korzhavyi *et al* [22], the value of β ranges from 0 to 1 in various studies (for specific details see [22]), in order to calculate alloy energetics that are consistent with experimental findings. Korzhavyi *et al* derive the value of 1.0 under assumptions which they consider to be consistent with the SS nature of the CPA. The picture regarding the derivation or use of this formula is further complicated by the fact that it has been 'derived' from considerations of ordered structures as well as within formalisms based on the study of disordered alloys within the CPA. However, the fundamental underpinnings of this approach are fairly constant, providing a straightforward approach to its analysis.

The difficulties associated with equation (3.1) are not related to the value of β but are of a fundamental nature. Basically, this expression is so ill defined as to be completely unreliable as a computational tool. In justifying this assertion, consider the following.

The magnitudes of the net charges entering this expression depends on the partition of a material into cells and can assume quite arbitrary values. If one derives these charges from studies of ordered structures, one can easily repartition these structures into Voronoi polyhedra that are neutral and, therefore, zero out any charge transfer and its effects. Alternatively, one can induce charge transfer of arbitrary magnitude even in a single-component system, say Cu, by dividing the material into cells of two different sizes so that one now has an 'alloy' consisting of charged cells. In both of these cases, one must be able to show that the electrostatic energy of the *ordered* system as calculated based on equation (3.1) is independent of the mode of partition or of the assignment of charge to particular cells. Since it is possible to show that in general equation (3.1) does not satisfy this requirement, it stops being a legitimate instrument of analysis. We now prove this assertion.

Consider an ordered linear chain (any structure would do, but the linear chain is simple to analyse) consisting of equally spaced alternating charges of value ± 1. Now, consider this structure to result from charge displacement, or charge transfer, originating from a system of neutral cells, whereby each distinct pair of neighbours exchanges charge of magnitude $\pm\frac{1}{2}$. That is to say, each cell originally contains equal amounts of positive and negative charge of magnitude $\frac{1}{2}$. Divide the structure into non-overlapping pairs of cells $(1, 2)$, $(3, 4)$, etc, and within each such set $(i, i + 1)$ let a positive charge of $\frac{1}{2}$ move from cell i to cell $i + 1$, while a charge of $-\frac{1}{2}$ moves from cell $i + 1$ to cell i. The resulting system is the alternating charge structure with which we started out, consisting of cells of net charges $Q_A = 1$ and $Q_B = -1$.

It is easy to show that the electrostatic energy of such a structure, represented by an alternating harmonic series, is equal to $2 \ln 2$. It is also easy to show that this energy is not given in general by the expression in equation (3.1). Furthermore, the energy of a *random* linear chain of net charges ± 1 present at equiatomic concentration vanishes identically, a result which also is *not* given correctly by equation (3.1). The vanishing of the electrostatic energy in this case follows immediately from the fact that for any given distance on the chain the positive contributions to the energy (associated with pairs of both positive or both negative charges) cancels exactly the negative contributions (associated with pairs of positive charge at one end and negative charge at the other). This shows the dangers inherent in basing a treatment of the Poisson field on charge transfer rather than on the charge itself.

In addition to these difficulties, other disadvantages are associated with the treatment of charge transfer based on the study of ordered structures as carried out so far. These studies involve systems at different concentrations and the mixing of information deriving from different systems is inappropriate. An atom of type A, say, in a binary alloy $A_{1-c}B_c$ of a given concentration is distinguishable from an atom of the same type in the alloy at a different concentration. To say that an atom of type A exhibits a net charge of amount δQ_A when it has z nearest neighbours at concentration $1 - c$ provides no information whatsoever about the corresponding charge transfer at concentration $1 - c'$. To this one must add the fact that volume is usually a function of concentration which implies that the volume assigned to an atom at a given concentration, and which defines the amount of charge in the cell, is not formally related to that at another concentration. Therefore, a single description of charge transfer obtained from different ordered structures at different concentrations is physically meaningless.

3.2. Corrections to the coherent-potential approximation

Several methods have been proposed for correcting the CPA results to account for charge-transfer effects in substitutionally disordered alloys. In one approach, Johnson and Pinski [23] suggested a CPA formulation associated with a multicomponent alloy, whose components were equal in number to the number of configurations of a nearest-neighbour shell as defined by the possible number of atoms of different species. For example, for a binary alloy based on an FCC lattice, each atom of type A (B) can have 13 distinct types of near-neighbour environment as defined by the presence of $0, 1, 2, \ldots, 12$ atoms of type A in the near-neighbour shell. Thus, in this treatment, one must consider a 26-component alloy. For reference purposes, we can refer to these 'atoms' with the numbers $1, 2, 3, \ldots, 26$, in some order.

The difficulties with this prescription are quite serious. First, the approximation is uncontrolled because it introduces correlations which are topologically prohibited. For example, the CPA condition is based on considering a 'real' atom embedded in an effective medium which carries information about *all* types of atom in the alloy. Thus, an atom of type 1, which we can take to be an atom of type A surrounded by 12 neighbours of type A, is allowed to be next to an effective atom which is made up from information about all types of atom, including atom of type, say, 26, which we can take to be an atom of type B surrounded by 12 B atoms. Similar unphysical correlations are introduced with respect to configurations that are much more prevalent than the two extreme configurations just mentioned. Because these configurations are incompatible, one cannot assess the effect of introducing them by any computational means (in contrast with the SS CPA which neglects the effects of correlations that *can* exist in the alloy and is thus amenable to examination of the effects of this neglect).

In other work, Korzhavyi *et al* [22] provide a prescription for correcting the potential on an atom of a given species α in a binary alloy by an amount V^α given by the expression

$$V^\alpha = e^2 \frac{Q_\alpha}{R_1} \qquad \alpha = \text{A or B}. \tag{3.2}$$

The electrostatic interaction of the system is then given by equation (3.1), but with $\beta = 1$. They show that this screened-impurity model (SIM) gives the same results as the so-called [23] screened CPA, provided that one assumes that the net charge of the impurity is completely screened by the charge in the nearest-neighbour shell and that the screening charge is equally distributed among these neighbours. The method is also similar in spirit to that used [24] to correct the results of a muffin-tin (MT) application of the CPA to Al–Li alloys and whose results for Al–Li alloys are shown below. Briefly described, it is possible at the end of a calculation to correct the electrostatic energy that one obtains in the CPA by redistributing the charge between near neighbours so that the cells (the atomic spheres) are neutral. In this approach, one treats the entire charge density, rearranged in a fashion that the equivolume atomic spheres are neutral, so that it avoids the pitfalls of a treatment that is based only on net charges. When applied to the case of Al–Li alloys, this approach yields results very similar to those obtained in the SIM. However, like the other methods mentioned above, it also is not a satisfactory treatment of alloy electrostatics for a number of reasons.

First, these methods provide a non-self-consistent correction to the results of the CPA which disqualifies it as a *bona-fide* theory of alloys. Second, they involve a non-physical distribution of charge that is not suggested by the calculation itself. Finally, they cannot always be relied upon to provide a proper improvement to alloy energetics. Thus, these methods, as well as any so far discussed, do not provide a satisfactory treatment for the electrostatic energy of a random alloy.

3.3. Perturbative methods

In a recent publication, Staunton *et al* [25] have suggested a perturbative correction to the electrostatic energy of an alloy. They have derived an expression for the energy of an ordered alloy which contains, among others, two main contributions: a band energy term, obtained in the so-called method of concentration waves or the $S^{(2)}$ approach [26], and a term which is of the form $\Gamma(Q_A - Q_B)^2$. The quantity Γ is independent of charge transfer and, according to these workers, reflects the underlying structure of the system including the degree of screening of an impurity charge provided by the valence electrons.

The expression obtained by Staunton *et al* is of a perturbative nature, at least this is the case with the band energy contribution occurring in it. Its purpose is to obtain the energy of an *ordered* alloy configuration from the energy of the random material as calculated within the CPA. The accuracy of such schemes hinges crucially on the accuracy of the CPA medium. It also assumes that the second-order corrections to the band energy due to the variation in the Fermi energy are negligible. In the case in which the CPA is applied to non-neutral cells, the resulting effective medium can be grossly inaccurate and the validity of a perturbation expansion must be seriously questioned. (The case of Al–Li alloys discussed in this paper provides an example of this occurrence.) The fact that calculations for the Cu–Zn system seem to give 'improved' results is not adequate justification. Because charge-transfer effects in this system are essentially non-existent, all treatments of this alloy that have appeared in the literature have given the same physical information. This implies that this system does not provide a particularly telling ground for testing a new method. Finally, an application of the expression to a simple model system such as the linear chain considered above can prove illuminating.

4. Self-consistent treatment within the coherent-potential approximation

The previous discussion has highlighted the difficulties inherent in calculating the electrostatic interaction in disordered alloys described in terms of non-neutral cells, particularly within the framework of the SS CPA. It has also indicated a possible approach to the problem, namely the use of charge-neutral cells in implementing the CPA. However, such an implementation cannot be carried out in an obvious way. When the cells (or spheres) are allowed to vary in size, it is no longer possible to arrange them on the sites of a single lattice without bringing up serious questions of overlap among cells. It is, therefore, necessary to invoke a new scheme for applying the CPA condition in this case.

Charge-transfer effects in the study of substitutional alloys are associated with the presence of an excess or a deficient number of electrons in the WS cells as defined by the lattice around atoms of different species. Although equivolume WS cells are the obvious choice in a monatomic material, their use in the study of multicomponent alloys can lead to considerable inaccuracies. The difficulties are associated with the calculation of the electrostatic interaction in the case of substitutionally disordered systems.

In developing our formalism, first we seek a unified and unique, fully self-consistent treatment of alloys that encompasses both the scattering aspects of the problem, embodied in the Schrödinger equation, as well as the electrostatic aspects, embodied in the Poisson equation. Second, the theory should lend itself naturally to analysis not only of the energetics of disordered alloys but also of other properties such as the nature of the electronic states and electronic transport. Third, it should have the required analytic properties, associated with the preservation of causality, and should satisfy fundamental sum rules, e.g. on the total charge, as well as behave properly in the limits of relevant physical parameters, such

as concentration. With regard to the last requirement, note that the zero-concentration limit is not to be identified with the single-impurity limit. (Any finite number of impurities in an infinite system corresponds to zero concentration. Thus, it is necessary to take limits as the concentration approaches zero from the finite side.) Finally, the method should allow the use of well established perturbative corrections to the CPA and the identification of effective cluster interactions for the study of the thermodynamic properties of an alloy. The CPA satisfies all physical requirements as the concentration vanishes, but it cannot be shown to be exact in the single-impurity limit. Since it is known that the CPA, at least in the case of neutral cells, satisfies all the above requirements, it is sensible to attempt its generalization to systems that exhibit charge-transfer effects. To do so, we shall formulate the CPA so that it allows the treatment of substitutionally disordered alloys in terms of neutral cells which must of necessity be of different volumes for different species.

We envisage the sites in a substitutionally disordered alloy as forming a number of lattices, each lattice being associated with each distinct combination of individual species. For example, we describe a binary alloy in terms of three lattices, an AA, a BB, and an AB lattice. Our goal is to formulate the Korringa–Kohn–Rostoker (KKR) CPA self-consistency condition under the more relaxed conditions of species-dependent lattice structures. These 'lattices' are not real in the sense that they do not determine directly the volume of the system. That is given uniquely by the volume occupied by the charge, so that it is determined as the average of volumes associated with the cells of different species in the system. The use of these lattices, however, which are also uniquely determined by the sizes assigned to the cells, allows one to use the entire construction of multiple-scattering theory and of the CPA so that overlap of adjacent cells is completely avoided.

At the same time, the resulting formalism represents a further approximation to that already embodied in the CPA. Namely, the structure of the system is replaced by the construction just described, as in the ordinary CPA the scattering of a real atom is replaced by the scattering of an impurity in the CPA medium. This second approximation becomes necessary in order to treat the Poisson field explicitly, which is an issue in the presence of charge-transfer effects. The configurational matrix formalism developed below can be readily adapted to the required extension of the CPA.

In order to obtain a multilattice or configurational matrix version of the KKR CPA, we must describe a method for integrating quantities in reciprocal space in order to obtain the corresponding quantities in site space. To this end, we note an interesting property between the lattice Fourier transforms of different lattice structures of the type needed here.

Consider two lattice structures, say 1 and 2, such that, for any two sites i and j in lattice 1, there exist a corresponding pair of sites in lattice 2, and such that intersite distances are proportional, $\boldsymbol{R}_{ij}^2 = f \boldsymbol{R}_{ij}^1$, with f being a real number. Thus the two lattices are connected by a uniform compression or expansion. This relation also characterizes the primitive vectors of the lattice so that the Brillouin zones (BZ) of the two lattice structures are related by the uniform compression (or expansion) $1/f$. Thus, there exists a unique one-to-one correspondence between the points in the first BZ of the two lattice structures. In fact, for $\boldsymbol{k}^\alpha$ in the first BZ of the αth lattice, $\alpha = 1, 2$, we have the relations

$$\boldsymbol{k}^\alpha \cdot \boldsymbol{R}_{ij}^\alpha = \boldsymbol{k}^\beta \cdot \boldsymbol{R}_{ij}^\beta \qquad \text{for all } \beta. \tag{4.1}$$

Furthermore, with $\underline{G}(\boldsymbol{R}_{ij}^\alpha)$ denoting the structure constants of the αth lattice, we have

$$\frac{1}{N} \sum_j \underline{G}(\boldsymbol{R}_{0j}^\alpha) \exp^{(\mathrm{i}\boldsymbol{k}^\alpha \cdot \boldsymbol{R}_{0j}^\alpha)} = \frac{1}{N} \sum_j \underline{G}(\boldsymbol{R}_{0j}^\alpha) \exp^{(\mathrm{i}\boldsymbol{k}^\beta \cdot \boldsymbol{R}_{0j}^\beta)}$$
$$= \underline{G}^\alpha(\boldsymbol{k}^\alpha). \tag{4.2}$$

Thus, the KKR structure constants of one lattice can be obtained as a Fourier transform over the first BZ of another. This result can be used in formulating a version of the KKR CPA in which charge-transfer effects are taken into account in a self-consistent way. We provide an explicit discussion for the case of binary alloys. Multicomponent alloys can be treated in a straightforward extension of the formulae obtained here to higher-dimensional matrices.

Now, following the lines of development presented in the previous paper, we cast the equation of motion for the scattering-path operator, $\underline{\tau}^{nm}$, in the matrix form

$$\underline{\tau}^{nm} = \underline{\mathbf{t}}^n \delta_{nm} + \underline{\mathbf{t}}^n \sum_k \underline{\mathbf{G}}(R_{nk})\underline{\tau}^{km}. \tag{4.3}$$

Here, the site-diagonal t-matrices are given by expressions similar to those in equation (3.26) of the preceding paper, but with $\underline{t}^\alpha$, the cell t-matrix for the potential cell at site n, replacing $(\underline{q}^\alpha)^{-1}$. Similarly, the scattering path operators and structure constants are matrices in configuration space. However, in contrast with the formalism of the previous paper, the structure constants are now assigned values that are consistent with the configurational lattices introduced in this approach.

In the spirit of the CPA, we now replace the site-dependent t-matrix by an effective configuration-independent quantity $\bar{\mathbf{t}}$ and, using the property of lattice Fourier transforms exhibited in equation (4.2), we solve for the effective medium scattering path operator in reciprocal space:

$$\bar{\underline{\tau}}(\mathbf{k}) = \left(\begin{bmatrix} \bar{\underline{t}}^{AA} & \bar{\underline{t}}^{AB} \\ \bar{\underline{t}}^{BA} & \bar{\underline{t}}^{BB} \end{bmatrix}^{-1} - \begin{bmatrix} \underline{G}^{AA}(\mathbf{k}) & \underline{G}^{AB}(\mathbf{k}) \\ \underline{G}^{BA}(\mathbf{k}) & \underline{G}^{BB}(\mathbf{k}) \end{bmatrix} \right)^{-1}. \tag{4.4}$$

Using matrix quantities to replace the effective t-matrix by the renormalized interactor of the effective medium, we can write the KKR CPA self-consistency condition in the form

$$\begin{bmatrix} c_A[\underline{m}^A - \bar{\underline{\Delta}}^{AA}]^{-1} & 0 \\ 0 & c_B[\underline{m}^B - \bar{\underline{\Delta}}^{BB}]^{-1} \end{bmatrix} = \begin{bmatrix} \bar{\underline{\tau}}^{AA} & 0 \\ 0 & \bar{\underline{\tau}}^{BB} \end{bmatrix}$$

$$= \frac{1}{\Omega_{BZ}} \int_{BZ} \mathrm{d}^3 k \left(\begin{bmatrix} \bar{\underline{\tau}}^{AA} & 0 \\ 0 & \bar{\underline{\tau}}^{BB} \end{bmatrix}^{-1} - \begin{bmatrix} \bar{\underline{\Delta}}^{AA} & \bar{\underline{\Delta}}^{AB} \\ \bar{\underline{\Delta}}^{BA} & \bar{\underline{\Delta}}^{BB} \end{bmatrix} \right.$$

$$\left. - \begin{bmatrix} \underline{G}^{AA}(\mathbf{k}) & \underline{G}^{AB}(\mathbf{k}) \\ \underline{G}^{BA}(\mathbf{k}) & \underline{G}^{BB}(\mathbf{k}) \end{bmatrix} \right)^{-1}. \tag{4.5}$$

Expressions for the Green function can be obtained through the relations established in the preceding paper. It might have become clear from our discussion in that paper that the last expression for the KKR CPA self-consistency condition can also be written in various forms, such as that which involves the product $\underline{\tilde{S}}^n \underline{C}^n$, rather than the t-matrix (or its inverse).

Two points remain to be clarified with respect to equation (4.5). First, the integrations occurring in it can be performed over any one of the three BZ, that are defined by the AA, the BB or the AB lattice. However, although the integration variable can vary only over a single zone, each of the structure constants must be properly evaluated in its own. Thus, the $\alpha\beta$ structure constants in an alloy should be constructed on the basis of a lattice parameter given by $a^{\alpha\beta} = \frac{1}{2}\left(a^{\alpha\alpha} + a^{\beta\beta}\right)$. This prescription gives the distance between the centres of two adjacent cells of types α and β and, when used to construct the structure constants, guarantees that two such cells in a full-cell treatment do not overlap. Second, equation (4.5) can easily be used to describe alloys in which charge-transfer effects extend over the first few coordination shells of the lattice. To do so it is necessary only to use the structure factors associated with the affected shells in setting up the structure constants of the lattices.

The significance of the role played by the lattices in configurational space deserves further discussion. It is tempting to apply this matrix formulation of the CPA to study the effects of lattice relaxation in cases in which atoms of given species are attracted or repelled in pairwise fashion away from their equilibrium lattice positions, but such a treatment is unwarranted and unphysical. The lattices in configuration space are not associated with real atomic positions and are set up only to eliminate (or to minimize) the effects of overlap. The matrix extension of the CPA is used here to treat the additional complications arising from the presence of the Poisson field which exhausts its utility.

4.1. Numerical results

In the remainder of this section, we present numerical results obtained in the application of the KKR CPA to FCC-based Al–Li alloys. We present results obtained within a MT approximation to the alloy potential as well as within an ASA. Within the ASA, we also implemented a version of the configurational matrix approach discussed here. This version consists in imposing the further condition that the structure constants associated with the AB lattice are the geometric mean (rather than the arithmetic mean) of those for the AA lattice and BB lattice. This approximation retains the main advantage of the configurational matrix formalism, namely the ability to control the effective overlap between adjacent spheres, while reducing the matrix form of the CPA to its ordinary 'scalar' version. The corresponding formal manipulations leading to this reduction have been presented in a previous publication [16]. Finally, the calculations in the ASA were carried out within a fully relativistic framework [27] because of our intent to provide a completely unified treatment of alloys that includes not only simple metals (where relativistic effects are unimportant) but heavy elements as well.

Figure 1 shows the concentration dependence of the mixing energy of Al–Li alloys, defined as

$$\Delta E = E_{alloy} - (1 - c)E_A - cE_B \tag{4.6}$$

where E_{alloy}, E_A and E_B are the equilibrium ground-state energies of the alloy and of its pure constituents A and B at concentrations $1 - c$, and c calculated at their equilibrium volumes V_{alloy}, V_A and V_B, respectively. The full squares in the figure denote the mixing energy as obtained in the non-relativistic MT version of the KKR CPA and show a strong tendency towards phase separation. At the same time, the MT approximation leads to rather large effects associated with the treatment of alloy charges for two main reasons. First, the cell charges that lie outside the MT spheres (the spheres inscribed in the WS cells) are non-negligible (of the order of half an electron) and can be strongly species dependent. The ordinary MT treatment averages these charges into a constant interstitial charge distribution before calculating the electrostatic part of the alloy energy.

Second, the WS cells in the MT calculations, including the charges inside the MT spheres and in the interstitial region, are found to be different from the nuclear charge, resulting in positively charged Al and negatively charged Li cells. The calculation of the electrostatic interaction in the alloy within the MT approximation is based on the fact that the cells are neutral on the *average*, resulting in possible inaccuracies with respect to the treatment of the interstitial charge and its interaction with the MT charges, as well as in the treatment of the interaction of the total charge in a cell with the rest of the charges. It is at this stage that the average of a product of charges is effectively being replaced by the product of their averages. One way to correct for the effects of this treatment in a non-self-consistent way is the following.

First, we assumed that the WS cells are spherical, subtracted the average of the electrostatic energy associated with the interaction of the constant interstitial charge with the MT charge and added the average interaction of the MT charge in a cell with its own interstitial charge. We shall refer to this correction as U_1. The mixing energy calculated with this type of correction is shown by the full circles in figure 1. The alloy still shows a tendency towards phase separation, but much more weakly than in the MT calculation. Proceeding further, we reassigned the charge in the interstitial region so that individual cells associated with different species are neutral. This was done assuming equivolume spheres around each atom, irrespective of species, and that the charge is spherically symmetric throughout. Also, the excess or deficiency in the reassigned charge was placed in the interstitial region. Consistent with this construction, we then subtracted the average of the intra cell interaction of the MT calculation and added the average of the intra cell interaction of the neutral spheres. In short, we subtracted the electrostatic interaction as calculated in the MT approximation and added the interaction calculated on the basis of equivolume neutral spheres. In this procedure it was found that the total correction for the equiatomic composition was nearly equal to twice U_1, so that $2U_1 = U_2$ was taken to be the value of the total correction throughout the concentration range.
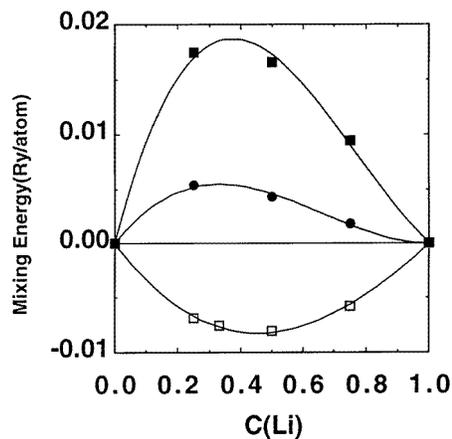

Figure 1. Mixing energy of Al–Li alloys versus Li concentration: ■, MT results; ●, non-neutral atomic spheres; □, neutral atomic spheres.

It is clear that the correction just described is not self-consistent since the reassignment of charge is done in a rather arbitrary fashion at the end of the calculation. It is not well justified and it is not suggested as a proper way of calculating alloy electrostatics. As is argued below, its value lies primarily in delineating the effects of charge transfer and pointing a way towards a fully self-consistent approach in accounting for them. In any case, this procedure results in a concentration dependence of the mixing energy depicted by the open squares in figure 1. These results are more in accord with experiment since at least in the region of low Li contents the alloy is stable with respect to phase separation.

Similar effects are found with the correction scheme just described in connection with the equilibrium volume of the alloy, as is indicated in figure 2. The MT results are given by the full squares in the figure and are clearly in contradiction with experiment since Al–Li alloys exhibit a slight volume contraction at small Li concentrations. The lattice parameter obtained when correcting for the interstitial charge only, called U_1 above, is indicated by the
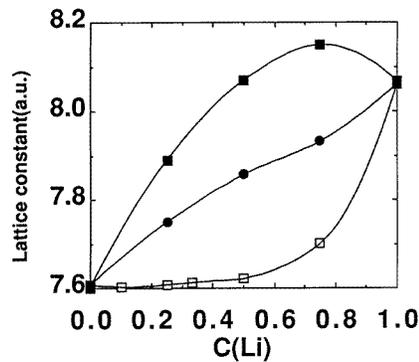
Figure 2. Equilibrium lattice parameter for FCC Al–Li alloys as a function of Li concentration calculated within the three different schemes described in the caption of figure 1.

full circles. A correction of U_2 type leads to a remarkably accurate variation (open squares) of the alloy lattice constant with concentration for a Li content less than or equal to $\frac{1}{4}$. Once again, these results should not be excessively relied upon as providing proof of a proper treatment of alloy energetics. Rather, they suggest that the energetics should be calculated in connection with charge neutral cells within a fully self-consistent theory. Within the SS CPA a formulation must be sought that allows its implementation with respect to charge-neutral cells. In fact, the need to use charge-neutral cells associated with individual alloy species has been suggested in previous publications [16, 18]. In those papers, however, the neutral spheres were centred on the sites of a rigid lattice which brings up serious questions of overlap effects. In the calculations described in the following two figures, these overlap effects are improved somewhat through the use of the lattices in configurational space. At the same time, it cannot be overstated that the full use of this approximation and a proper assessment of its validity require its implementation in connection with the full matrix formalism and a full-cell treatment of charges and potentials.

The mixing energy as a function of concentration calculated within the ASA version of the CPA is shown in figure 3. The open circles depict the results obtained in an ASA calculation associated with non-neutral spheres of equal volume and based on a single lattice. It is seen that the elimination of the poor treatment of the interstitial charge, associated with the MT approach, results in a mixing energy that is considerably smaller than that obtained in the MT case (full squares in figure 1). However, it is still positive, which makes the random solid solution or random alloy unstable against phase separation. When the calculation is repeated in terms of neutral spheres still based on a single lattice but having different volumes for the Al and Li species, larger than the ASA volumes for Al and smaller for Li, the mixing energy assumes the form shown by the full circles in figure 3. The mixing energy now becomes negative, indicating the stability of the alloy against phase separation, but it is much too large. One conceivable source of error is the increased overlap of the Al spheres which exists at high Al contents and whose volume becomes larger than the ASA volume.

The open squares in figure 3 depict the concentration dependence of the mixing energy when the calculation is carried out within the framework of the species-dependent lattices in configuration space. These results also indicate the stability of the alloy against phase separation but the magnitude of the energy is improved considerably with respect to those associated with a single lattice. Judging from the behaviour exhibited in the non-self-

consistent calculations, and from the well known results that ASA calculations tend to yield smaller volumes than when corrected for overlap effects, this improvement can be ascribed to the relief of the overlap of the larger Al spheres allowed by the configurational lattice formulation of the CPA.
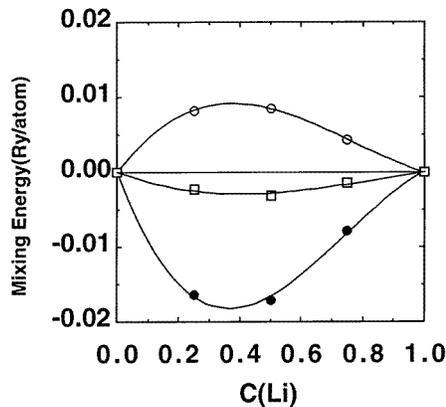

Figure 3. Mixing energy of Al–Li alloys as a function of Li concentration calculated within the ASA version of the CPA: $\bigcirc$, non-neutral equivolume atomic spheres; $\bullet$, neutral spheres on a rigid lattice; $\square$, neutral spheres on configurational lattices.
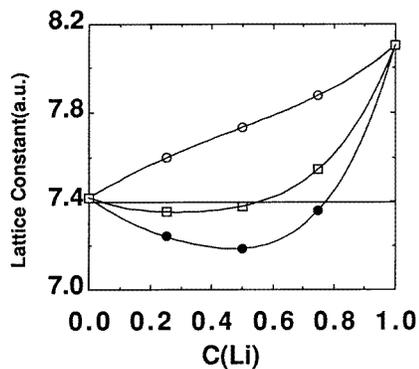

Figure 4. Variation in lattice parameter of Al–Li alloys as a function of Li concentration in the three different schemes described in the caption of figure 3.

Finally, figure 4 shows the results for the variation in the lattice parameter of the random alloys with concentration obtained within the three various ASA calculations described above. An ASA CPA calculation based on equivolume and charged spheres on a single lattice yields the results identified by the open circles in the figure. It is to be noted that the behaviour of these volumes with concentration is essentially indistinguishable from those obtained with the U_1-type correction in the MT calculations, shown by open circles in figure 2. (The absolute values of the lattice parameters in an ASA calculation are expected to be somewhat smaller than those obtained within a MT treatment.) This is not surprising since the corrected MT results correspond to equivolume charged atomic spheres, being different from the ASA results only because they are not self-consistently obtained. The

similarity of the curves indicates that indeed charge-transfer effects can be large enough to mask any effects of a self-consistent treatment. At the same time, the self-consistent results should be viewed as the more reliable, as well as being associated with a 'proper' alloy theory.

The full circles in figure 4 indicate the concentration variation in the alloy lattice parameter when the spheres are allowed to become neutral but are kept centred on the sites of a single lattice. The results obtained when the lattices in configuration space are introduced are shown by the open squares in the figure. These are much more in agreement with experimental results than either of the other two curves in the figure. For the reasons presented above, they are also closely related to the fully corrected MT results shown by the open squares in figure 2.

It is to be noted that, based on equation (3.1), Korzhavyi *et al* [7] obtained a concentration dependence of the lattice parameter of Al–Li alloys that is essentially indistinguishable from that of the fully corrected MT results, shown by the open squares in figure 2. This indicates the importance of the electrostatic interaction in the study of disordered alloys, as well as that so-called charge-transfer effects do not require a description in terms of charge fluctuations which, as argued above, are in fact non-physical. They can be fully accounted for through a treatment of the total charge in the system which can be accomplished by viewing the system as a collection of neutral cells. In the case of ordered materials, the use of neutral cells does not present formal problems. In the case of disordered alloys treated within the SS CPA, the use of neutral cells can be implemented within the configurational matrix approach discussed in the previous paper.

5. Discussion and conclusions

The difficulties encountered in the treatment of the electrostatics of disordered alloys, especially in attempts to correct the results obtained within the CPA, are a direct consequence of the fundamental difference in the character of the Schrödinger equation and the Poisson equation, the first being of the homogeneous kind and the second of the inhomogeneous kind. These differences manifest themselves in the locality of the former and the (in principle) infinite extent of the latter. Within the ordinary version of the CPA, the two fields are treated quite differently which precludes a combined approach unless the CPA itself is modified in some way (one possible modification being that of the configurational matrix approach described above). It is instructive to compare and contrast the two fields and their treatment in connection with disordered materials afforded within the CPA framework.

As far as the Schrödinger equation for a disordered alloy is concerned, the CPA yields an effective medium described by an effective cell scattering matrix. In doing so, the CPA neglects statistical fluctuations in the local environment of a site. These fluctuations can always be defined with respect to the CPA effective medium and methods for their evaluation can be devised, either based on a perturbative approach, or by the direct treatment of clusters of sites embedded in the CPA medium. In this case, the meaning of fluctuations as deviations from an 'average' medium is well defined and allows studies based on methods designed to account for them.

The Poisson equation, on the other hand, does not lend itself to a mean-field treatment. There is no CPA analogue for the Poisson equation. One cannot define effective multipole moments, the analogues of an effective scattering matrix in the scattering solutions, with respect to which fluctuations can be studied. This is another point brought out by consideration of the example of the linear chain of disordered positive and negative charges. The example was mentioned to emphasize the resistance of the Poisson equation to a mean-

field treatment. Therefore, local environment effects with respect to charge fluctuations cannot be profitably used in the analysis of the electrostatics of disordered alloys, at least not within the ordinary version of the CPA.

In realistic calculations that result in charge-neutral cells (or atomic spheres) for individual atomic species, the Poisson equation requires no additional treatment. Note that, within the ASA, the potential of a neutral cell vanishes outside the sphere and, as far as the electrostatics part of the treatment is concerned, atoms of various species are indistinguishable! In a full-cell approach, there are higher multipole moments to be considered but these are usually small and converge very rapidly (at least for cubic systems). Therefore, numerically, the distinction between different species essentially vanishes (exactly within the ASA) when neutral cells are used. We arrive once again at the conclusion drawn above that charge fluctuations should not be associated with local environment effects, but rather with the partition of a system into cells. For this reason, charge transfer can be zeroed out by redefining cell sizes. In contrast, regardless of partitioning, the meaning of fluctuations in scattering strength remains a valid concept, emphasizing the fundamental difference in the two fields and the need for their independent treatment.

As a result of the preceding discussion, it seems that the most useful way to treat the Poisson equation within a CPA formalism is to avoid having to treat it at all. This is accomplished by the configurational matrix approach presented here. The result is a promising theory of alloys free of *ad-hoc* corrections, which makes unique predictions about all physical properties of a material connected to its electronic structure. At the same time, it would also be of interest to explore possibilities of studying alloys within a cluster theory which would allow a possibly more satisfactory and accurate treatment of the charge itself rather than any ill-defined charge fluctuations.

Acknowledgments

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