PART I

Phase Stability: First Principles Theory

The Electronic Structure and Phase Stabilities of Metallic Alloys

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Abstract

Condensed matter consists of positively charged atomic nuclei and the electron 'glue' which holds them together. Although it is attractive to attempt to model it by neutral atoms interacting via relatively weak pairwise 'effective interactions' in general this can not be done with impunity. Usually, such phenomenological approaches break down due to proliferation of adjustable parameters. Evidently this undermines both the predictive and interpretative power of the analysis. Hence, there is no substitute to forging a parameter-free and quantitative theory of the complex degenerate Fermi liquid 'glue' to complement phenomenological calculations. Such theory is the general aim of 'first-principles' calculations of the electronic structure. This talk will concern past present and future first-principles calculations relevant to the state of compositional order in metallic alloys. Special attention will be paid to phase instabilities induced by Fermi Surface effects.

1 Introduction

The problem of alloy Phase Diagrams [1] is one of the oldest in Physics, Chemistry and Metallurgy, and it is of abiding technological interest. Thus, it is not surprising that there are many approaches to it. One can seek to correlate crystal structure and compositional order with significant parameters like atomic sizes, electronegativities and electron per

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atom ratios. This was the approach of Hume-Rothery [2] Darken and Gurry [3] and this is the line of argument followed by Miedema [4] and Pettifor [5] in much of their current work. Alternatively, one can attempt to fit the available thermochemical data to fairly flexible, but thermodynamically sound, mathematical representations of the free energy and, so to speak, extrapolate information from the known regions of thermodynamic phase space to those not yet explored experimentally. This is the strategy which underlies most of the work that appears on the pages of *Calphad* edited by Kaufman [6]. It is probably fair to say that, for the time being, practically all technologically useful phase diagrams are produced this way. A third, more microscopic, line of reasoning assumes that the total energy of the system is a sum over effective, pairwise interactions and proceeds to implement the corresponding statistical mechanical calculations. Over the past decade activity based on this approach was dramatically enhanced by the realization that, at least for short range interactions, the problem can be solved virtually exactly by the Cluster Variational Method (CVM) [7] or MonteCarlo simulations [8]. Consequently, much progress is being made along this line. Finally, and inevitably, there is the first principles point of view which faces up to the fact that condensed matter consists of positively charged atomic nuclei and the electron *glue* between them. Apart from its intrinsic interest the legitimacy of this endeavor derives from the fact that in the above phenomenological approaches adjustable parameters often proliferate to such an extent that intelligibility and predictive power is undermined. Although progress in applying first principles methods has been slow, with the advent of the self-consistent KKR–CPA [9] it has been sufficiently real that first principles calculations can now usefully complement the other approaches.

For maximum effect we advocate the adoption of a loose combination of all four of the above points of view. We stress the word loose because they don't fit together in a quantitative fashion. For instance, in first principles calculations, electronegativity, size effect and electron per atom ratio are taken into account on equal footing, however, they do not correspond to uniquely definable quantities which could be identified with corresponding parameters of the phenomenological schemes. Similarly, it is not possible to extract pair potential parameters from the first principles calculations without considerable equivocation. Nevertheless, the field has become sufficiently mature to permit the making of qualitative and even semi-quantitative connections which illuminate the subject. In the interest of efficient presentation, we shall review only the theory of compositional order based on the fully self-consistent KKR–CPA method and bypass the very active field of semi-phenomenological tight–binding model calculations. For a treatment of progress made in this way the reader is referred to Ducastelle [10]. We shall also have to forgo describing methods, like that of Connoly and Williams [11] which involve first principles calculations for ordered ground states only and introduce thermal fluctuations via effective, model Hamiltonians.

The structure of our presentation is highlighted by the section headings which we hope are self-explanatory.

2 The self-consistent KKR–CPA

The Density Functional Theory (DFT) is, in principle, an exact method for dealing with an electron system in the field of the atomic nuclei. The Local Density Approximation (LDA) to it has proved be a very reliable guide to the energetics of ordered solids such as pure metals or intermetallic compounds [12]. The self-consistent KKR–CPA [9] is an adaptation of the LDA to systems with cellular disorder, for example, random alloys.

To describe the theory we must begin by recalling what DFT–LDA means for random alloys. Evidently we must solve the usual self-consistent, Schrödinger like, Kohn-Sham equations:

$$\left[-\nabla^2 + \sum_i v_i(\vec{\mathbf{r}})\right] \psi_n(\vec{\mathbf{r}}) = \epsilon_n \psi_n(\vec{\mathbf{r}}) \tag{1}$$

for all configurations and average the relevant observables over the appropriate ensemble of configurations.

To be specific let us introduce an occupation variable ξ_i which takes on the value 1 if there is an A atom at the lattice site labelled i and 0 if the site is occupied by a B atom. To specify a configuration we must then assign a value to these variables ξ_i at each site. Let us denote a full set of such values, and therefore a configuration, by $\{\xi_i\}$. Then the potential function $v_i(\vec{\mathbf{r}})$ in eq. 1 may be written as

$$v_i(\vec{\mathbf{r}}) = v\left(\vec{\mathbf{r}} - \vec{\mathbf{R}}_i; [n(\vec{\mathbf{r}}; \{\xi_i\})]\right) \tag{2}$$

where the functional $v(\vec{\mathbf{r}} - \vec{\mathbf{R}}_i; [n])$ is given by the LDA, $\vec{\mathbf{R}}$ is the position vector of the i-th nuclei in the i-th unit cell, and $n(\vec{\mathbf{r}}; \{\xi_i\})$ is the charge density for a given configuration $\{\xi_i\}$.

According to Density Functional Theory eq. 1 must be solved self-consistently for each configuration $\{\xi_i\}$. Namely, for an initial charge density $n(\vec{\mathbf{r}}; \{\xi_i\})$ we must calculate the potential functions $v(\vec{\mathbf{r}} - \vec{\mathbf{R}}_i; [n])$ and solve eq. 1 for the energy eigen-function $\psi_n(\vec{\mathbf{r}})$ and eigen-value ϵ_n. Then we must evaluate

$$n(\vec{\mathbf{r}}; \{\xi_i\}) = \sum_n |\psi_n(\vec{\mathbf{r}})|^2 f(\epsilon_n) \tag{3}$$

and compare the result with the starting charge density. If they agree within a prescribed limit the solution is self-consistent. If not the procedure is to be repeated with the new charge density as the starting guess until convergence.

Formally, the next step is to calculate some physically interesting observable, for example the ground state energy $E_0^{\mathrm{LDA}}(\{\xi_i\})$ and average it:

$$\overline{E} = \sum_{\{\xi_i\}} P(\{\xi_i\}) E_0^{\mathrm{LDA}}(\{\xi_i\}) \tag{4}$$

with respect to a suitable probability distribution, $P(\{\xi_i\})$. For an alloy, in thermal equilibrium, in the Born-Oppenheimer approximation,

$$P(\{\xi_i\}) = \frac{1}{Z} e^{-\beta E_0(\{\xi_i\})} \tag{5}$$

where

$$Z = \sum_{\{\xi_i\}} e^{-\beta E_0(\{\xi_i\})}. \tag{6}$$

Evidently, it is impossible to implement the above sequence of calculations as they stand. The principal difficulties are: solving eq. 1 for arbitrary configurations with no translational symmetry and performing the sums over all configurations in eq. 4 and eq. 6. The theory we are about to describe solves both of these problems, albeit approximately, in the spirit of a mean-field approximation.

As a first step we consider the homogeneous self-consistent KKR-CPA. It consists of the assumption that

$$P(\{\xi_i\}) = \prod_i p(\xi_i) \tag{7}$$

and a subtle inversion of the process of averaging and self-consistency. The simple product form on the right hand side of eq. 7 means that the ξ's are independent random variables. Moreover, the fact that all the local distributions are the same implies that on the average all the sites are the same. That is to say the system is translationally invariant on average. To be specific $p(\xi_i)$ may be parameterised by the concentration c of the A species in the following form

$$p(\xi_i) = c\xi_i + (1-c)(1-\xi_i). \tag{8}$$

The next step is to replace, in the spirit of a mean-field theory, the local potential function in eq. 2 by its average over all the occupation variables save the one referring to the site i, namely $\langle v_i(\vec{r}-\vec{R}_i;[n(\vec{r};\{\xi_i\})])\rangle_{i,\alpha}$

$$\begin{aligned}\langle v_i(\vec{r}-\vec{R}_i;[n(\vec{r};\{\xi_i\})])\rangle_{i,\alpha} &= \overline{v}(\vec{r}-\vec{R}_i;\xi_i) \\ &= \xi_i\overline{v}^A(\vec{r}-\vec{R}_i;\overline{n}^A,\overline{n}_0)+ \\ &\quad\ (1-\xi_i)\overline{v}^B(\vec{r}-\vec{R}_i;\overline{n}^B,\overline{n}_0)\end{aligned} \tag{9}$$

where the two potential functions on the right hand side are the LDA potential functionals evaluated at the partially averaged densities

$$\overline{n}^\alpha = \langle n(\vec{r};\{\xi_i\})\rangle_{i,\alpha} \tag{10}$$

inside the muffin-tin sphere surrounding the site i and at the average charge density $\overline{n}$ elsewhere.

The procedure is now clear: we start with a set of partially averaged charge densities $\overline{n}^A$ and $\overline{n}^B$, calculate the corresponding partially averaged potential functions $\overline{v}^A$ and $\overline{v}^B$ and distribute these in all possible ways on the sublattice according to the distribution given in eq. 7; then solve the Schrödinger equations given in eq. 1 for the partially averaged charge densities $\overline{n}^A$ and $\overline{n}^B$ as defined in eq. 10; this procedure is, then, repeated until the starting and the final charge densities are the same within prescribed limits. Evidently, the above scheme inverts the order in which charge self-consistency and averaging over configurations is achieved.

Note that as yet we have not specified how the Schrödinger equation for the random potential is to be solved for the partially averaged charge densities in eq. 10. Given the mean-field description for the local potentials $\overline{v}^A$ and $\overline{v}^B$ and the fact that the occupation variables ξ_i are independent random variables it is natural to perform this calculation within the Coherent Potential Approximation (CPA) [13]. The potential functions are constructed in the form of non-overlapping, spherically symmetric potential wells whose effect on the motion of an electron is treated using the Korringa-Kohn-Rostoker multiple scattering theory. Hence, the complete scheme is referred to as the self-consistent KKR–CPA.

To facilitate our exposition we note that instead of the Schrödinger equation in eq. 1 the actual KKR–CPA scheme deals with the corresponding equation for the Greens function:

$$\left[-\epsilon-\nabla^2+\sum_i\overline{v}(\vec{r}-\vec{R}_i;\xi_i)\right]G_{\sigma\sigma}(\vec{r},\vec{r}';\epsilon)=\delta(\vec{r}-\vec{r}') \tag{11}$$

where σ refers to the spin of the electron being described. The CPA, whose principal merit is that it can deal with arbitrarily large differences between $\overline{v}^A$ and $\overline{v}^B$ in eq. 9, is a prescription for calculating both the configurationally averaged Greens function $\langle G_{\sigma\sigma}(\vec{r},\vec{r}';\epsilon)\rangle_{i,\alpha}$ and the partially averaged Greens functions $\langle G(\vec{r},\vec{r}';\epsilon)\rangle_{i,A}$ and $\langle G(\vec{r},\vec{r}';\epsilon)\rangle_{i,B}$, where the meaning of the partial averaging is the same as in eq. 9. Indeed, the local charge densities $\overline{n}^A$ and $\overline{n}^B$ are calculated from the latter two of these quantities using the usual formula

$$\overline{n}^\alpha(\vec{\mathbf{r}}) = -\frac{1}{\pi}\int f(\epsilon)\Im\langle G(\vec{\mathbf{r}},\vec{\mathbf{r}};\epsilon)\rangle_{i,\alpha}d\epsilon. \tag{12}$$

Information concerning the averaged energy eigen-value spectra can also be extracted from the above, variously averaged, Greens functions. For instance the partially averaged densities of states are given by

$$\overline{n}^\alpha(\epsilon) = -\frac{1}{\pi}\int_{\Omega_i}\Im\langle G(\vec{\mathbf{r}},\vec{\mathbf{r}};\epsilon)\rangle_{i,\alpha}d\vec{\mathbf{r}} \tag{13}$$

where the integral is over the i-th unit cell in which there is an α-type atom. Also, the most complete description of the spectra is provided by the Bloch spectral function

$$A^B(\vec{\mathbf{k}},\epsilon) = \sum_{i,j} e^{i\vec{\mathbf{k}}\cdot(\vec{\mathbf{R}}_i-\vec{\mathbf{R}}_j)}\int_{\Omega_i}\Im\langle G(\vec{\mathbf{r}}+\vec{\mathbf{R}}_i;\vec{\mathbf{r}}+\vec{\mathbf{R}}_j;\epsilon)\rangle d\vec{\mathbf{r}}. \tag{14}$$

For the sake of clarity it is useful to note that for an ordered system

$$A^B(\vec{\mathbf{k}},\epsilon) = \sum_\nu \delta(\epsilon-\epsilon_{\vec{\mathbf{k}},\nu}) \tag{15}$$

where $\vec{\mathbf{k}}$ is the Bloch wave number and ν is the band index. For disordered alloys these δ-function peaks broaden out into peaks with finite width, which are usually interpretable as finite inverse life-times, and finite heights whose position in the $\vec{\mathbf{k}}$, ϵ space traces out the band structure. It should be stressed that while $\vec{\mathbf{k}}$ is not a good quantum number for a given configuration $\{\xi_i\}$, it does correspond to the translational symmetry, of the average lattice. Namely $A^B(\vec{\mathbf{k}},\epsilon)$ is periodic and has the Brillouin zone of the unoccupied lattice. When the states are extended, the peaks of $A^B(\vec{\mathbf{k}},\epsilon)$ are well separated and we have a band structure in a similar sense as for pure systems but with a disorder induced life-time associated with each state. Presently, we shall have occasion to display the Bloch spectral function at the Fermi energy ϵ_F in various $\vec{\mathbf{k}}$-directions calculated for Cu$_c$Pd$_{1-c}$ alloys using the KKR–CPA.

3 The configurationally averaged total energy in the KKR–CPA

Of course, from the point of view of Phase Diagram the most interesting feature of the above theory is its ability to yield quantitative configurationally averaged total energies $\overline{E}$. The formula for $\overline{E}$ is a non trivial combined consequence of the Density Functional Theory in the LDA and stationary properties of CPA. As will be discussed, at length, in a forthcoming publication [14] it takes the form

$$\overline{E} = cE_J[\overline{n}^A,\overline{n}_0,\overline{n}] + (1-c)E_J[\overline{n}^B,\overline{n}_0,\overline{n}] \tag{16}$$

where E$_J$ is the functional derived by Janak [15] for ordered systems with crystal potential in the muffin-tin form. $\overline{n}^A$ and $\overline{n}^B$ are the partially averaged charge densities defined in eq. 10, $\overline{n}$ is the fully averaged charge density and $\overline{n}_0$ is the same but in the interstitial region. A remarkable feature of eq. 16 is that, thanks to the use of CPA, $\overline{E}$ retained the variational properties characteristic of $E[n]$ for pure systems. Namely

$$\frac{\partial\overline{E}}{\partial\overline{n}^A} = 0 \quad \text{and} \quad \frac{\partial\overline{E}}{\partial\overline{n}^B} = 0. \tag{17}$$

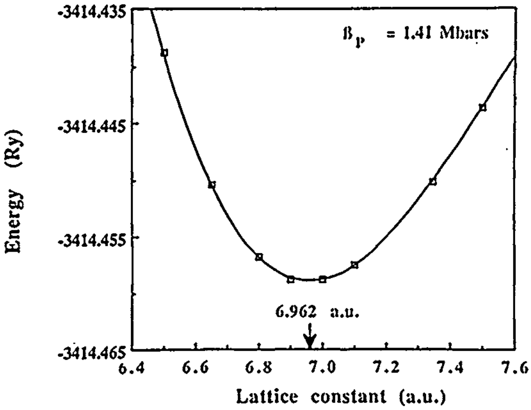

Figure 1: The variation of the alloy total energy (Ry) with lattice constant (a.u.) for FCC $Cu_{0.5}Zn_{0.5}$ alloy. A cubic least-squares fit gives a minimum energy of -3414.45888 Ry at 6.963 a.u. and a bulk modulus of 1.41 Mbars. This plot is typical for the FCC CuZn alloys.

This feature certainly is one of the reasons for the success of the KKR-CPA theory for the total energy. Some of these we shall now recount. In fig. 1 show the total energy E as a function of the lattice parameter a calculated for FCC $Cu_{0.5}Zn_{0.5}$ alloy. The minimum at $a_E = 6.962$ au is within a 0.5% of the experimentally determined equilibrium value. Moreover, the calculated pressure versus a curve crosses zero at $a_p = 6.933$ au which is in very satisfactory agreement with a_E determined from the total energy calculation. The most remarkable aspect of these calculations is that their consistency and accuracy appear to be those usually associated with similar calculations in pure systems.

Similar calculations at various concentrations in the FCC (α-phase) yield a lattice parameter versus concentration curve shown in fig. 2. A particularly pleasing feature of

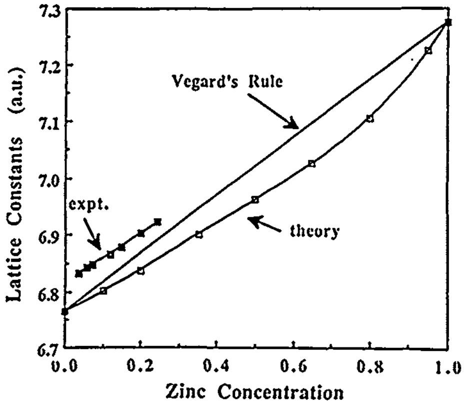

Figure 2: Concentration variation of the lattice constant (a.u.) for the FCC CuZn alloys.

the generally good agreement between theory and experiment is the fact that $\left(\frac{\partial a}{\partial c}\right)_{c=0} =$

0.0036 per atomic %Zn which deviates from the prediction of Vegard's rule of 0.0052 per atomic %Zn but agrees with the experimental result of 0.0036 per atomic %Zn. We note that the experimental determination was at T=300K but the estimated differential thermal expansion is small and the agreement is real at the 0.5% level.

Furthermore, the calculations of the bulk moduli also yield fairly satisfactory agreement with the experiment: theory gives $\beta_E = 1.67$ Mbars while the measured value is 1.42 Mbars for the 50–50 alloy. This is also in line with the agreements achieved by LDA calculations for pure systems.

From the point of view of the phase diagram the most interesting results coming out of the above calculations are the energies of mixing

$$\Delta E^{\rm mix} = \overline{E} - cE^A - (1-c)E^B \tag{18}$$

where E^A and E^B are the ground state energies of the pure A and pure B metals with the same lattice. Our results for $\Delta E^{\rm mix}$ vs concentration c are shown in fig. 3. The negative sign of $\Delta E^{\rm mix}$ implies an ordering tendency which is a feature of the rather complicated $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ phase diagram (Hansen [16]). Interestingly $\Delta E^{\rm mix}$ is not strictly parabolic and this suggests a complex phase diagram. A detailed discussion of this will be given elsewhere (Johnson*et al* [14]).

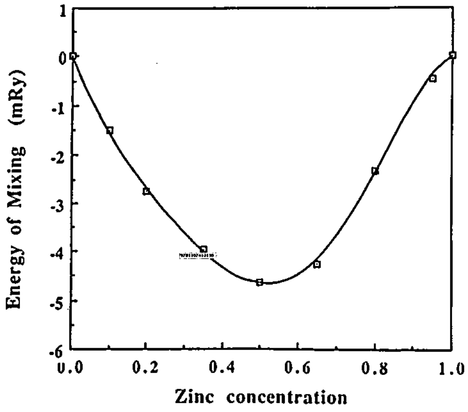

Figure 3: Concentration variation of the heats of mixing (mRy) for FCC CuZn.

We now turn to our next subject which is concentration fluctuations about the homogeneous state discussed above.

4 Order–Disorder transformation

It is a fairly straightforward matter to argue that a mean-field theory of compositional order has two parts: the first is a statement that there is a generalized grand potential, $\Omega^{\rm MF}(T, \nu, \{c_i\})$, which is a function of temperature T, chemical potential difference ν and all the local concentrations $\{c_i\}$ (defined as the thermodynamic averages of the occupation variables $\{\xi_i\}$, namely $c_i = \langle \xi_i \rangle$); the second is the assertion that at its minimum with respect to arbitrary variations in the local concentration variables $\{c_i\}$, $\Omega^{\rm MF}$ is the thermodynamic grand potential. Thus the state of compositional order is found by solving the Euler-Lagrange equations:

$$\frac{\partial \Omega^{\mathrm{MF}}}{\partial c_i} = 0. \tag{19}$$

Quite generally, Ω^{MF} can be decomposed into an ideal entropy contribution which is due to non-interacting fluctuations of concentrations, as in regular solution theory, and an interaction function Ω^{int}. For a pair interaction model, described by the Hamiltonian $\mathcal{H} = -\frac{1}{2}\sum_{ij} \grave{v}_{ij}\xi_i\xi_j$, where, in a self-explanatory notation $\grave{v}_{ij} = \grave{v}_{ij}^{AA}+\grave{v}_{ij}^{BB}-2\grave{v}_{ij}^{AB}$, $\Omega^{\mathrm{int}} \equiv \langle\mathcal{H}\rangle_0 = -\frac{1}{2}\sum_{ij} \grave{v}_{ij}c_ic_j$. Thus in our electronic model it is natural to take $\Omega^{\mathrm{int}}(\{c_i\}) = \langle\Omega_\epsilon\{\xi_i\}\rangle_0$ where $\langle\rangle_0$ means averaging with respect to the inhomogeneous product distribution

$$P(\{\xi_i\}) = \prod_i p_i(\xi_i) \tag{20}$$

and $\Omega_\epsilon(\{\xi_i\})$ is the grand potential of the electrons for the configuration specified by $\{\xi_i\}$. Evidently, the single site distribution functions, $p_i(\xi_i)$, which now vary from site to site, are the generalizations of $p(\xi_i)$ in eq. 8, i.e.

$$p_i(\xi_i) = c_i\xi_i + (1-c_i)(1-\xi_i). \tag{21}$$

Finally our approximation to $\langle\Omega_\epsilon\{\xi_i\}\rangle_0$ is the configurationally averaged grand potential given by the inhomogeneous KKR–CPA $\Omega^{\mathrm{CPA}}(\{c_i\})$. In short our mean-field theory of compositional order is encapsulated by the equations [17]

$$\begin{aligned} \Omega\,(T,\nu,\{c_i\}) \;&=\; \Omega^{\mathrm{CPA}}(\{c_i\}) \\ &+\; \mathrm{k_B T}\sum_i (c_i \ln c_i + (1-c_i)\ln(1-c_i)) \\ &-\; \sum_i \nu_i c_i \end{aligned} \tag{22}$$

and

$$\left(\frac{\partial \Omega}{\partial c_i}\right) = \mathrm{k_B T}\ln\frac{c_i}{1-c_i} + \left(\frac{\partial \Omega^{\mathrm{CPA}}}{\partial c_i}\right) - \nu_i = 0 \tag{23}$$

where the chemical potential difference ν_i is allowed to vary from site to site for formal purposes only, and the basic conditions which define the inhomogeneous KKR–CPA theory [17].

These latter are the straightforward generalizations of the usual CPA idea to the case where the probability that a site, say i, is occupied by an A atom, namely c_i, differs from site to site. Although, this inhomogeneous KKR–CPA recipe can not be implemented numerically, it is a very useful formal device because it can be expanded about the homogeneous limit, i.e. $c_i = \bar{c}\ \forall i$, and it allows the calculation of the derivatives

$$S_i^{(1)} = \left(\frac{\partial \Omega^{\mathrm{CPA}}}{\partial c_i}\right)_{c_i=\bar{c}\ \forall i} \tag{24}$$

and

$$S_{ij}^{(2)} = \left(\frac{\partial^2 \Omega^{\mathrm{CPA}}}{\partial c_i \partial c_j}\right)_{c_i,c_j=\bar{c}\ \forall i} \tag{25}$$

where $\bar{c}$ is the uniform concentration of the high temperature disordered phase.

The significance of $S^{(1)}$ is provided by eq. 23. As was pointed out by Györffy and Stocks [18] the second derivative is the mean-field approximation to the Orstein-Zernicke direct correlation function [19] and it plays a variety of important roles in the theory of compositional order.