Order and Disorder in Metallic Alloys [and Discussion]

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Order and disorder in metallic alloys

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Self-consistent ‘band theory’, based on density functional theory, is a useful approach to describing the electron glue which holds solids together. However, its powerful group theoretic and numerical techniques cannot be deployed for disordered states of matter. The self-consistent KKR-CPA is an analogous method which is able to deal with some of these interesting cases. In particular, we show how it describes random metallic alloys, treating all the classic Hume-Rothery factors: size-effect, electronegativity and electrons per atom ratio $(e:a)$ on more or less equal footing and from first principles. Moreover, we use the KKR-CPA framework to analyse the instability of the disorder state to compositional ordering processes and hence provide a first principle description of the forces which drive order–disorder transformations.

1. Introduction

The electronic structure of random crystalline metallic alloys is an important chapter in the quantum theory of solids (Hume-Rothery & Coles 1969; Mott & Jones 1936). After atoms, molecules and ordered crystalline solids this is the next most tractable problem of positively charged nuclei and the ‘electron glue’ between them. Moreover, it is the simplest non-trivial example where the theme of order–disorder is fully developed. In short the electronic states have new features and they drive novel phenomena such as phase separation and compositional ordering. We review the current state of our first principles’ understanding of the electronic structure and the way it determines the compositional short- and long-range order (de Fountain 1979; Kchaheturyan 1986).

Central to our discussion below are two assumptions: one is that of a rigid lattice and the other is that specifying the occupancy variable ξ_i (which takes on the value 1 if there is an A atom at the ith site and 0 if the atom at $\boldsymbol{R}_i$ is the B type) for all sites defines all compositional configurations. The first of these may be relaxed in favour of a symmetry statement, that on average the system is invariant under a set

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of translations which define a lattice, without seriously affecting the conceptual framework we are about to describe. The second, which is essentially the adiabatic theorem, can be relinquished only at the expense of an entirely new start involving diffusion. In short we consider configurations specified by the sets $\{\xi_i\}$ and average over all such sets with appropriate weights.

Traditionally, the study of electronic states in random alloys always followed that for pure metals and order intermetallic compounds with a lag, reflecting the technical difficulties of solving the Schrödinger equation without the full support of the Bloch theorem (Elliott *et al.* 1974; Ehrenreich & Schwartz 1976). One of the points we emphasize here is that recently the work on random alloys has caught up with that for ordered systems in the sense that we can now base our description of the electronic structure of each configuration $\{\xi_i\}$ on the local density approximation (LDA) to the density functional theory (DFT). Namely, for each configuration $\{\xi_i\}$, we consider the Kohn–Sham equation for the Greens function:

$$\left(\epsilon+\nabla^2-\sum_i v_\sigma^{\mathrm{LDA}}(\boldsymbol{r}-\boldsymbol{R}_i;\{\xi_i\})\right)G_{\sigma\sigma}(\boldsymbol{r},\boldsymbol{r};\epsilon)=\delta(\boldsymbol{r}-\boldsymbol{r}'),\tag{1}$$

where each potential well, centred at the atomic nuclei, is described by the LDA potential functional (Kohn & Vashista 1983), $v_{\mathrm{LDA}}^{\mathrm{eff}}(\boldsymbol{r}-\boldsymbol{R}_i;[n(\boldsymbol{r};\{\xi_i\}])$ and the charge density, $n(\boldsymbol{r};\{\xi_i\})$, is given by

$$n(\boldsymbol{r};\{\xi_i\})=-\frac{1}{\pi}\sum_\sigma\int \mathrm{d}\epsilon f(\epsilon)\,\mathrm{Im}\,G_{\sigma\sigma}(\boldsymbol{r},\boldsymbol{r};\epsilon).\tag{2}$$

Above, as usual, $f(\epsilon)$ stands for the Fermi function, $f(\epsilon)=(\exp\{\beta(\epsilon-\mu)\}+1)^{-1}$ at the inverse temperature $\beta=(k_{\mathrm{B}}T)^{-1}$ and electronic chemical potential μ, and σ is the spin label.

Thus, the starting point for our arguments is the following ‘Gedanken’ procedure: solve (1) and (2) self-consistently for a fixed configuration $\{\xi_i\}$, then, evaluate the DFT formula for the grand potential:

$$\Omega_e(\{\xi_i\})=\Omega_e[n(\boldsymbol{r};\{\xi_i\})]\tag{3}$$

and calculate the partition function for the combined electron nuclei system:

$$Z=\sum_{\{\xi_i\}}\exp\{-\beta(\Omega_e(\{\xi_i\})-\sum_i v_i\xi_i)\},\tag{4}$$

where v_i is the local chemical potential difference $v_i=v_i^{\mathrm{A}}-v_i^{\mathrm{B}}$ for the two species of nuclei. As usual, v_i is allowed to vary from site to site for formal purposes only. Finally, the ensemble of configurations, $\{\xi_i\}$, is defined by the distribution function

$$P(\{\xi_i\})=Z^{-1}\exp\{-\beta(\Omega_e-\sum_i v_i\xi_i)\}.\tag{5}$$

2. A first principles mean-field theory of compositional order

Although the above programme is not tractable as it stands, its mean field theoretic version is. We demonstrate, by using non-trivial examples, that this is a dramatic step forward in understanding the basic physics of metallic alloys.

The mean field approximation to the theory specified by equations (1)–(4) has three parts (Kohn & Vashista 1983; Gyorffy & Stocks 1983; Gyorffy *et al.* 1989).

The first is the usual assumption of a form for the free energy (grand potential) Ω, as a function of the local concentration configurations:

$$\Omega\,(T, v;\{c_i\}) = \Omega_e(\{c_i\}) + k_B T \sum_i (c_i \ln c_i + (1-c_i)\ln(1-c_i)) - \sum_i v_i c_i, \tag{6}$$

where c_i is the thermal average of ξ_i, consistent with the form of (6) (e.g. $c_i = -\partial\Omega/\partial v_i$), and

$$\Omega_e(\{c_i\}) = \langle \Omega_e\{\xi_i\}\rangle_0. \tag{7}$$

To be consistent with the simple form of the entropy contribution in (6) the average $\langle\ \rangle_0$ is to be taken with respect to the inhomogeneous product distribution

$$P_0(\{\xi_i\}) = \prod_i P_i(\xi_i) \tag{8}$$

for which each factor is parametrized by the local concentration c_i as follows:

$$P_i(\xi_i) = c_i\,\xi_i + (1-c_i)\,(1-\xi_i). \tag{9}$$

Finally, the state of compositional order is determined by finding the minimum of the grand potential, in (6), as a function of the local concentrations. Namely, at a given temperature T and chemical potential difference $v(=v_i\,\forall i)$ the equilibrium concentration configuration $\{\bar{c}_i\}$ is the solution of the Euler–Langrange equation:

$$(\partial\Omega/\partial c_i)_{\{\bar{c}_i\}} = 0. \tag{10}$$

The second and third part of the statement, which constitutes the mean field theory, has to do with the calculation of the average electronic grand potential specified by equations (7)–(9).

In the spirit of the LDA and the mean field theory the second part simplifies the local potential function in (1) by replacing it by its local, partial average,

$$\bar{v}(\boldsymbol{r}-\boldsymbol{R}_i;\xi_i) = \xi_i\, v^{\mathrm{A}}(\boldsymbol{r}-\boldsymbol{R}_i;[\bar{n}^{\mathrm{A}}(\boldsymbol{r}),\bar{n}(\boldsymbol{r})]) + (1-\xi_i)\, v^{\mathrm{B}}(\boldsymbol{r}-\boldsymbol{R}_i;[\bar{n}^{\mathrm{B}}(\boldsymbol{r}),\bar{n}(\boldsymbol{r})]), \tag{11}$$

where $\bar{n}^{\mathrm{A}}(\boldsymbol{r})$ and $\bar{n}^{\mathrm{B}}(\boldsymbol{r})$ are the partly averaged charge densities, $\bar{n}(\boldsymbol{r})$ is the fully averaged charge density:

$$\bar{n}(\boldsymbol{r}) = c\bar{n}^{\mathrm{A}}(\boldsymbol{r}) + (1-c)\,\bar{n}^{\mathrm{B}}(\boldsymbol{r}) \tag{12}$$

and the potential functionals $v^{\alpha}(r-R_i;[\bar{n}^{\alpha}(\boldsymbol{r}),\bar{n}(\boldsymbol{r})])$ are the usual LDA functional using $\bar{n}^{\alpha}(\boldsymbol{r})$ for the contributions from the ith unit cell and $\bar{n}(\boldsymbol{r})$ for the contributions from all the other unit cells. Evidently, α is A or B. Note that for the sake of clarity we have assumed that we are working in the disordered state where all A sites are equivalent and hence all A sites are characterized by the same partly averaged charge density $\bar{n}^{\alpha}(\boldsymbol{r})$, and potential function $\bar{v}^{\mathrm{A}}(r-R_i;\bar{n}^{\mathrm{A}}(\boldsymbol{r}),\bar{n}(\boldsymbol{r}))$. Clearly, the equivalent statement applies for the B sites.

The final, and third, part splits into two logically separate instructions: the first is to solve

$$\left(\epsilon + \nabla^2 + \sum_i \bar{v}(r-R_i;\xi_i)\right) G(\boldsymbol{r},\boldsymbol{r};\epsilon) = \delta(\boldsymbol{r}-\boldsymbol{r}') \tag{13}$$

for the averaged and partly averaged Greens functions and charge densities

$$\bar{n}^{\alpha}(\boldsymbol{r}) = -\frac{1}{\pi}\int \mathrm{d}\epsilon\, f(\epsilon)\ \mathrm{Im}\,\langle G(\boldsymbol{r},\boldsymbol{r};\epsilon)\rangle_0^{i\alpha}, \tag{14}$$

calculate the new potentials using (11), and repeat the procedure until convergence. The second is to use the coherent potential approximation (CPA) (Elliott *et al.* 1974; Ehrenreich & Schwartz 1976) for calculating the averages and hence take for $\Omega_e(\{c_i\})$ in (7) $\Omega_e^{\mathrm{CPA}}(\{c_i\})$ (Gyorffy *et al.* 1989).

Note that the first of these instructions interchanges the order of the self-consistency procedure demanded by DFT and the statistical averaging over the ensemble of configurations. Evidently, this is one of the features of the scheme which renders it tractable. The second instruction is also worthy of comment. Clearly the CPA is the natural approximation to use because, as it is made explicit by (8), the occupation variables are statistically independent and under such circumstances the CPA is known to be the mean field theory of disorder (Schwartz & Sigga 1972). Moreover, the self-consistent CPA algorithm which is implied by the above procedures have been fully implemented for realistic, muffin-tin, crystal potentials by the SCF-KKR-CPA method (Stocks & Winter 1984). This is the principle computational advance which makes the proposed calculations a practical proposition.

To highlight the physical content of the above first-principles mean field theory, we note that the solution of (10) in the disordered state is $\bar{c}_i = \bar{c}\,\forall i$. If the solution takes on any other pattern we speak of long-range order. Regions of the v, T plane, where solutions of different symmetry are of the lowest free energy, are separated by lines of phase boundaries and the totality of these constitutes the alloy phase diagram. Short-range order, on the other hand, is described by various derivatives of Ω with respect to the chemical potential. For example the Warner–Cowley short-range order parameter α_{ij} is given by the relation

$$\alpha_{ij} = \frac{1}{c_i(1-c_i)}(\langle \xi_i \xi_j\rangle - \langle \xi_i\rangle\langle \xi_j\rangle) = \frac{k_{\mathrm{B}}T}{c_i(1-c_i)}\left(\frac{\partial \Omega}{\partial v_i\,\partial v_j}\right)_{v_i = v\forall i}. \tag{15}$$

A particularly useful quantity is the direct correlation function

$$S_{ij}^{(2)} = (\partial \Omega_e^{\mathrm{CPA}}\{c_i\}/\partial c_i\,\partial c_j)_{\{\bar{c}_i\}}. \tag{16}$$

For instance, in the disordered state the lattice Fourier transform of α_{ij}, $\alpha(\boldsymbol{k})$, which is measured in diffuse scattering experiments, is given by

$$\alpha(\boldsymbol{k}) = k_{\mathrm{B}}T/(k_{\mathrm{B}}T - c(1-c)\,S^{(2)}(\boldsymbol{k})), \tag{17}$$

where $S^{(2)}$ is the lattice Fourier transform of $S_{ij}^{(2)}$ defined in (16).

3. The self-consistent field Korringa–Kohn and Rostaker coherent potential approximation [SCF-KKR-CPA]

Thus, for very general reasons, detailed in the previous section, we need to solve (13) for the partly averaged charge densities defined in (14). Note that this is a particularly simple example of electrons in disordered potential. It is often referred to as the case of cellular disorder and the CPA is a well-established method for dealing with it (Elliott *et al.* 1974; Ehrenreich & Schwartz 1976). This fact lands a solid foundation to the theory of random substitutional alloys which other random systems such as liquids and glasses do not possess.

Until recently (Kudrnovsky *et al.* 1989), of all the band theory methods like FLAPW, LMTP, KKR only the latter has been adopted for applications to disordered systems. In fact the multiple scattering version of the KKR proved eminently suitable for implementing the basic ideas of the CPA for random substitutional alloys (Gyorffy & Stocks 1979).

In fact the conceptual framework is very simple: sites described by the potential well corresponding to $v^{\alpha}(r-R)$ scatter electrons according to the partial wave scattering amplitudes

$$f_l^{\alpha}(\epsilon) = (1/2\mathrm{i})\,(\exp\,[\mathrm{i}2\delta_l^{\alpha}(\epsilon)]-1), \tag{18}$$

where $\delta_l^{\alpha}(\epsilon)$ is the usual scattering phase shift which describes the effect of a potential at the origin on the outgoing spherical waves, and we are looking for the electronic structure determined by the fundamental equation of multiple scattering. In a form most suitable for our present purposes it is given by

$$\sum_{L''l} (-\epsilon^{\frac{1}{2}} f_{il}^{-1}\,\delta_{il}\,\delta_{L,L''} - G_{L,L''}(\boldsymbol{R}_i - R_l;\epsilon))\,\tau_{L''L'}^{lj} = \delta_{LL'}\,\delta_{ij}, \tag{19}$$

where L stands for both the polar and azimuthal quantum numbers l and m respectively, $G_{L,L''}(\boldsymbol{R}_i - R_l;\epsilon)$ is the real space KKR structure constant which describes the propagation of free spherical waves of angular momentum L from site to site and $\tau_{LL'}^{ij}(\epsilon)$ is the scattering path operator (Gyorffy & Stocks 1979) which relates an incident wave of angular momentum L to the site j to an outgoing wave of angular momentum L' from the site i. Evidently for the random potential problem at hand $f_{i,l}^{-1} = \xi_i f_{\mathrm{A},l}^{-1} + (1-\xi_i) f_{\mathrm{B},l}^{-1}$.

An important feature of (19) is the separation of the scattering power at the scattering centres described by the scattering amplitudes $f_{i,l}(\epsilon)$, and the geometrical arrangements of such centres which determine the otherwise potential-independent structure constants $G_{LL'}(\boldsymbol{R}_i - \boldsymbol{R}_j;\epsilon)$. Note that the former appears only on the site diagonal part of (19). In the language of tight-binding model hamiltonians, this means the problem at hand corresponds to site diagonal randomness only. Interestingly, this is the case in spite of the fact that the scattering amplitudes $f_{\mathrm{A},l}$ and $f_{\mathrm{B},l}$ can correspond to bands of widely different widths. In other words, remarkably, the KKR-CPA treats on equal footing random alloys of metals with very different band position, band width and hybridization without introducing explicit off-diagonal randomness (Gyorffy & Stocks 1979).

The actual KKR-CPA procedure, based on (19), is very straightforward; we seek an effective (coherent) scattering amplitude which describe the average Greens function. It is the solution of the CPA condition which, for the KKR model, works out to be

$$c_i\,\tau_{LL'}^{\mathrm{A},ij}(\epsilon) + (1-c_i)\,\tau_{LL'}^{\mathrm{B},ij}(\epsilon) = \tau_{LL'}^{\mathrm{C},ij}(\epsilon), \tag{20}$$

where $\tau_{LL'}^{\alpha,ij}(\epsilon)$ is the site diagonal solution of (19) with an α impurity of $\boldsymbol{R}_i$ in the coherent potential lattice and $\tau^{\mathrm{C},ij}$ is the solution when all the sites are described by the effective scattering amplitudes $f_{i,\mathrm{C};L}(\epsilon)$.

Once (20) has been solved for $f_{i,\mathrm{C};L}(\epsilon)$ and $\tau_{LL'}^{\alpha,ij}(\epsilon)$ the partly averaged charge densities are to be calculated using the formula (Gyorffy & Stocks 1979):

$$\bar{n}^{\alpha}(\boldsymbol{r}) = -\frac{1}{\pi}\sum_{L}\int \mathrm{d}\epsilon f(\epsilon)\,Z_L^{\alpha}(\boldsymbol{r};\epsilon)\,Z_{L'}^{\alpha}(\boldsymbol{r};\epsilon)\ \mathrm{Im}\ \tau_{LL'}^{\alpha,ij}(\epsilon), \tag{21}$$

where $Z_{\mathrm{L}}^{\alpha}(\boldsymbol{r};\epsilon)$ is the regular, radial solution for an α-type muffin-tin potential well. In principle the above procedure can be iterated to self-consistency. It should be stressed that while the fundamental equation of inhomogeneous KKR-CPA given in (20) is the formal bases for calculating the generalized grand potential $\Omega_e^{\mathrm{CPA}}(\{c_i\})$ it can be solved only in the homogeneous limit where $c_i = \bar{c}\forall i$. Nevertheless, (20) can be used to derive computationally tractable expressions (Gyorffy & Stocks 1983) for the direct correlation function given in (16).

Before drawing this brief summary of our theory to a close, we comment on the nature of the electronic structure as described by the KKR-CPA.

In general, for a disordered system the wave vector $\boldsymbol{k}$ is not a good quantum number. Moreover, in the generic case, like a liquid or a glass, on the average the system is translationally invariant and hence the relevant wave vectors comprise all of $\boldsymbol{k}$-space. Namely the Brillouin zone is of infinite extent. Under these circumstances one is tempted to abandon the use of $\boldsymbol{k}$-space altogether in favour of real space methods like cluster or supercell calculations (Zunger *et al.* 1990). However, the cellular disorder of crystalline random alloys is an intermediate case between ordered crystals and the topologically disordered systems mentioned above. Here, the ensemble of configurations is invariant under the discrete set of translations which defines the underlying lattice and this introduces a periodicity in $\boldsymbol{k}$-space. That is to say, there are Brillouin zones of finite extent and the phase space to be considered is reduced to one of these. Of course, $\boldsymbol{k}$ is still not a good quantum number since the translational symmetry applies only on the average. Nevertheless, it turns out to be a surprisingly useful parameter. To make the best use of it one defines the Bloch spectral function

$$A_{\mathrm{B}}(\boldsymbol{k};\epsilon) = -\frac{1}{\pi}\sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{k}(\boldsymbol{R}_j-\boldsymbol{R}_i)}\int_{\Omega_i} \mathrm{d}r^3\, \mathrm{Im}\,\langle G(r+R_j, r+R_i;\epsilon)\rangle, \tag{22}$$

where the integral is over the ith unit cell whose volume is Ω_i. Within the KKR-CPA it is quite straightforward to evaluate the Bloch spectral function, which is automatically periodic in $\boldsymbol{k}$ space, and it gives the most complete account of the electronic states of a random alloy.

For an ordered system $A_{\mathrm{B}}(\boldsymbol{k};\epsilon)$ is given by a set of delta function peaks at $\epsilon = \epsilon_{\boldsymbol{k}}$, v, the Bloch energy eigenvalues for the band index v. Naturally, for disordered systems these peaks broaden out and their width can be interpreted as the inverse lifetime of the state specified by $\boldsymbol{k}$ and v. As an example we show, in figure 1, the Bloch spectral function at the Fermi energy ϵ_{F} in the ΓXWKWXΓ plane of the Brillouin zone for the very interesting $\mathrm{Cu}_{76}\mathrm{Pd}_{24}$ alloy system. Clearly, there is a Fermi surface well defined on the scale of its linear dimensions. Furthermore, it has interesting features, like the pronounced flat sheet perpendicular to the ΓK direction, and these can be measured in 2^{d} angular correlation of (position) annihilation radiation (ACAR) experiments (Berko 1979).

4. The configurationally averaged total energy

The above is one of the first useful results that comes out of a SCF-KKR-CPA calculation. The formula for it is a non-trivial, combined consequence of DET in the LDA and the stationarity property of the CPA. Nevertheless, it takes the following simple form (Johnson *et al.* 1990):

$$\bar{E} = cE_J[\bar{n}^{\mathrm{A}}, \bar{n}_0] + (1-c)\,E_J[\bar{n}^{\mathrm{B}}, \bar{n}_0], \tag{23}$$

where E_J is the total energy functional derived by Janak (1974) for ordered systems with the crystal potential in the muffin-tin form, $\bar{n}^{\mathrm{A}}(\boldsymbol{r})$ and $\bar{n}^{\mathrm{B}}(\boldsymbol{r})$ are the partly averaged local charge densities defined in (14), $\bar{n}(\boldsymbol{r})$ is the fully averaged charge

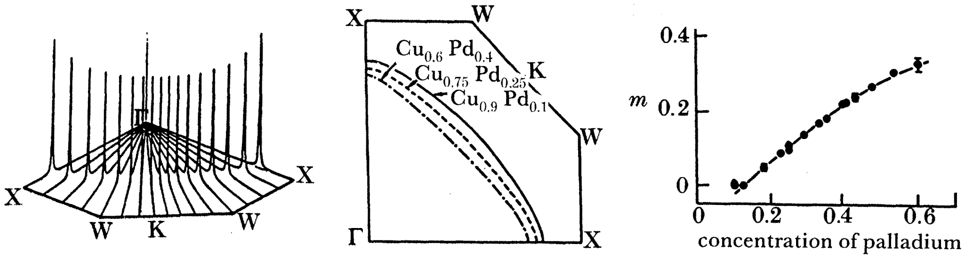

Figure 1. (*a*) The Bloch spectral function $A(\boldsymbol{k}; \epsilon_F)$ at the Fermi energy ϵ_F in the ΓXWKWXΓ plane of the Brillouin zone for the $Cu_{0.75}Pd_{0.25}$ alloy. (*b*) Evolution of the calculated Fermi surface with concentration c. (*c*) Variation of the incommensurability $m = 2(\sqrt{2} - 2k_F(011))$ with concentration.

Figure 2

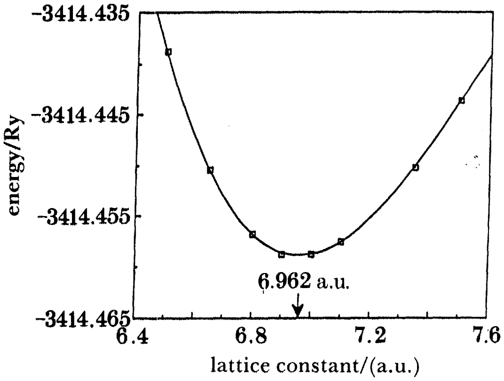

Figure 3

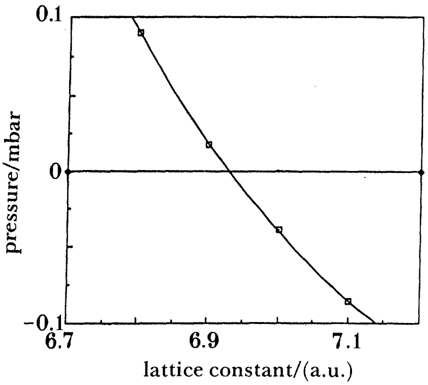

Figure 2. The variation of the configurationally averaged total energy (in rydbergs) with lattice constants (in atomic units) for the FCC $Cu_{0.5}Zn_{0.5}$ alloy. A cubic least-squares fit gives a minimum energy of -3414.45 Ry at 6.93 a.u. and a bulk moduli of 1.41 mbar (1.41×10^{11} Pa).

Figure 3. The variation of the alloy pressure (in rydbergs) with lattice constant for FCC $Cu_{0.5}Zn_{0.5}$. The zero pressure point is at $a_P = 6.93$ a.u. and the bulk moduli is 1.41 mbar (1.41×10^{11} Pa).

density and $\bar{n}_0$ is the same but in the interstitial region. A similar formula applies for the pressure (Johnson *et al.* 1990). A remarkable feature of (23) is that, due to the use of the CPA, E has similar variational characteristics as the total energy in the ordered state. Namely,

$$\delta \bar{E} / \delta \bar{n}^A(\boldsymbol{r}) = 0; \quad \delta \bar{E} / \delta \bar{n}^B(\boldsymbol{r}) = 0. \tag{24}$$

This property is, certainly, one of the principal reasons for the success of the SCF-KKR-CPA in predicting the total energy as a function of concentration.

In figure 2 we present our calculated $\bar{E}$ as a function of the lattice constant for the FCC $Cu_{0.50}Zn_{0.50}$ random alloy. The minimum at $a_E = 6.96$ a.u.† is within 5% of the experimentally determined equilibrium value. Moreover, the calculated pressure against 'a' curve, shown in figure 3, crosses zero at $a_P = 6.93$ a.u., which is in very satisfactory agreement with a_E determined from the total energy calculation. Thus the consistency and accuracy of these calculations are comparable with those achieved in similar calculations in ordered systems (Moruzzi *et al.* 1978).

Repeating the above calculations for various concentrations yields the lattice parameter against concentration curve shown in figure 4. A particularly pleasing

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† 1 a.u. ≈ 5.3×10^{-11} m.

Figure 4

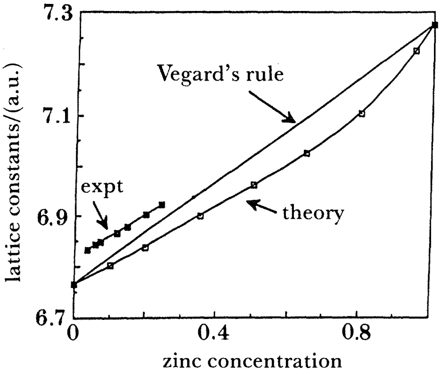

Figure 5

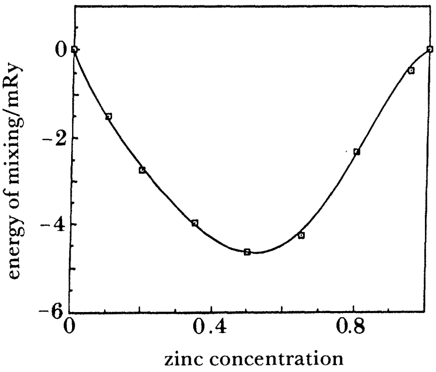

Figure 4. The variations of the lattice constant a with concentration as calculated by the SCF-KKR-CPA. For comparison we also show the prediction of Vegard's rule.

Figure 5. The calculated heats of mixing at various concentrations for the FFC Cu_cZn_{1-c} alloys.

feature of the generally good agreement between the theory and experiment is the fact that $(\partial a/\partial c)_{c=0} = 0.0036$ per at. % Zn which deviates from the prediction of the Vegard's rule of 0.0052 per at. % Zn but agrees with the experimental result of 0.0036 per at. % Zn. While it should be stressed that the experimental determination was at $T = 300$ K the thermal expansion coefficient for this alloy is small and hence the agreement is real at the 0.5% level.

Another quantity of interest is the heat of mixing given by

$$\Delta E^{\mathrm{mix}} = \bar{E} - cE^{\mathrm{A}} - (1-c)\,E^{\mathrm{B}}, \tag{25}$$

where E^{A} and E^{B} are the ground state energies of the pure A and pure B metals, respectively, on the alloy lattice. Our calculated values of ΔE^{mix} at various concentrations are shown in figure 5. The negative sign of ΔE^{mix} implies a tendency to order which is consistent with the rather complicated phase diagram which features various order phases (Hansen 1958). Indeed the fact that ΔE^{mix} is not a parabolic function of c suggests such a phase diagram.

More details concerning these calculations are found in the recent paper of Johnson *et al.* (1990).

5. Order–disorder transformations

One of the most intriguing complex of ordering phenomena takes place in the Cu rich $Cu_{1-c}Pd_c$ alloys (Oshima & Watanabe 1976; Ceder *et al.* 1989). For instance, in the high-temperature disordered phase diffuse scattering experiments find in $\alpha(\boldsymbol{q})$ [110] superlattice peaks, split into four peaks. This implies a tendency to form concentration waves incommensurate with the underlying lattice (Sato & Toth 1965). Moreover, these peaks move apart as c changes from 0.12 to 0.4, where they disappear (Oshima & Watanabe 1976). The first success of the first-principle mean field theory described in §2 was to give a microscopic explanation of these observations (Gyorffy & Stocks 1983; Gyorffy *et al.* 1989). In fact, the calculations identified the parallel flat sheets of the Fermi surface, whose presence can be deduced from the Bloch spectral function displayed in figure 1, as the electronic driving mechanism behind the ordering process. Examples of the calculated four peaked $\alpha(\boldsymbol{k})$ are shown in figure 6.

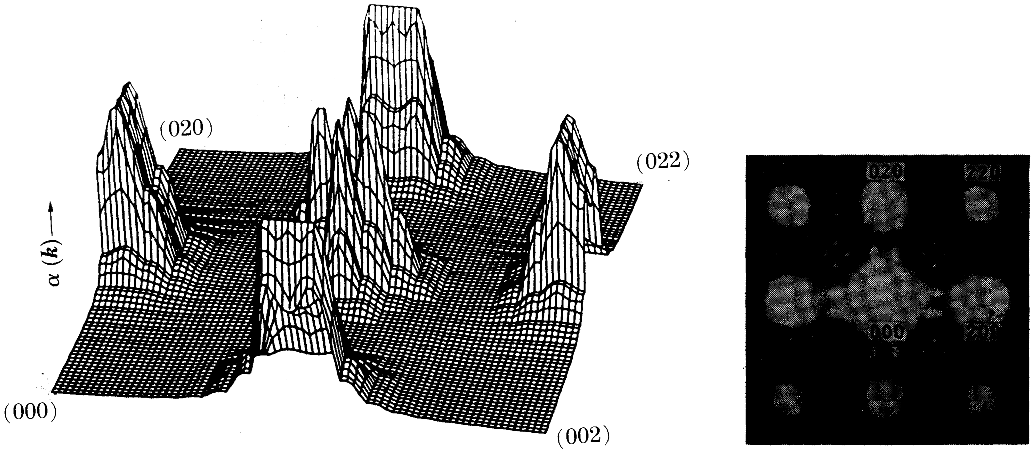

Figure 6. The concentration–concentration correlation function $\alpha(\boldsymbol{k})$ (the Warren–Cowley short-range order parameter) as calculated in the first-principles mean field theory based on the SCF-KKR-CPA in the plane containing the reciprocal lattice points 000, 020, 022, 002 for various $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloys.

Figure 7

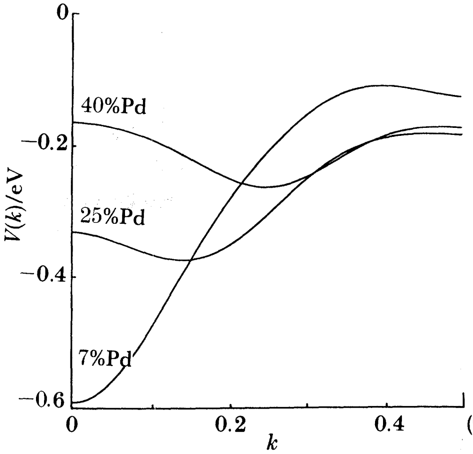

Figure 8

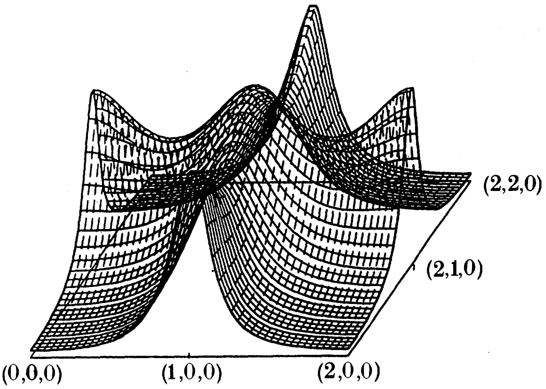

Figure 7. The calculated effective pair interaction parameter $\boldsymbol{v}(\boldsymbol{k})$ along the XW segment (k, 10) in the first Brillouin zone for 7%, 25% and 40% Pd in $\mathrm{Cu}_c\mathrm{Pd}_{1-c}$ alloys.

Figure 8. The calculated Warren–Cowley short-range order parameter $\alpha(\boldsymbol{k})$ in the $k_z = 0$ plane for $T = 1.1\ T_0$, where T_0 is the theoretical ordering temperature. The peaks at the X-points indicate that the alloy will order into a $Q = (1, 0, 0)$ concentration wave ($\mathrm{L1}_0$) state for $T < T_0$.

As is well known, with certain caviats notwithstanding, the direct correlation function $S^{(2)}(\boldsymbol{k})$, from which $\alpha(\boldsymbol{k})$ is calculated according to (7), can be regarded as the lattice Fourier transform of an effective pairwise, interchange, potential $\tilde{v}(\boldsymbol{k})$ [$\equiv v^{\mathrm{AA}}(\boldsymbol{k})+v^{\mathrm{BB}}(k)-2v^{\mathrm{AB}}(\boldsymbol{k})$]. To display the subtle ways the ordering tendency changes in these alloys we plot $S^{(2)}(\boldsymbol{k};c) = \tilde{v}(\boldsymbol{k};c)$ for various concentrations in figure 7. Recently, using these curves, in figure 7 and the mean field theory Cedar *et al.* (1991) have constructed the full, very complex, low-temperature phase diagram featuring lock in transitions into high-order commensurate phases, in good qualitative agreement with experiments.

Another recent application of the method is to the Pt_c–Ni_{1-c} alloy system. These alloys represent a serious problem for theories based on simple tight-binding models of the electronic structure because they predict a trend according to which alloys with nearly half-filled d-band order and those for which ϵ_F falls near the bottom or the top of the effective d-band phase separate (Heine & Samson 1983; Teleglia & Ducastelle 1987). Experimentally Pt_c–Ni_{1-c} is found to order, contradicting the above trend governed by the band filling or electron per atom ratio e/a.

Surprisingly, the first principles mean field theory based on the SCF-KKR-CPA predicts ordering in agreement with experiments. We show $S^{(2)}(k)$ in the $k_z = 0$ plane in figure 8. The sharp rise of $S^{(2)}(\boldsymbol{k})$, from the Γ point to the zone boundary, can be interpreted as a robust tendency to order in agreement with the experiments of Dahmani *et al.* (1985). The reason for this dramatic difference between the tight-binding model calculations and the SCF-KKR-CPA-based theory is very interesting. Analysis of our results suggest that ordering in this system is due to the size effect which overpowers the competing e/a effect. In other words our first principles calculation correctly reproduces the metallurgical rule of thumb according to which alloys of large and small atoms order (on an FCC lattice into an $L1_2$ structure).

In the language of tight-binding model hamiltonians big and small atoms, on the same lattice, give rise to large and small overlap integrals and hence bandwidths. This in turn causes off-diagonal randomness which, in general, is difficult to treat. The key to the success of the first principles calculation is the SCF-KKR-CPA method which treats site-diagonal, site-off-diagonal and hybridization randomness on equal footing.

In summary we stress that our first principles mean field theory, while subject to limitations due to the neglect of certain correlations, treat all the classic Hume-Rothery factors which determine the state of compositional order, namely electron per atom ratio, size effect and electronegativity, on equal footing and without adjustable parameters. The most reassuring aspect of the above Pt_c–Ni_{1-c} example is that it appears to be an adequate theory of the relative significance of these factors even when they drive the ordering and clustering tendency in the opposite direction.

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Discussion

H. Rafii-Tabar (*Department of Materials, Oxford University, U.K.*). Is there a simple relationship between the A–B interaction on the one hand and the A–A and B–B interactions on the other hand in Professor Gyorffy's calculations?

B. L. Gyorffy. This is a first principles electronic theory in which there are no pair potentials as such. The direct correlation function $S^{(2)}(\boldsymbol{k})$ may, however, be interpreted (in the mean spherical approximation) as the interchange energy $v(\boldsymbol{k}) = v^{\mathrm{AA}}(\boldsymbol{k}) + v^{\mathrm{BB}}(\boldsymbol{k}) - 2v^{\mathrm{AB}}(\boldsymbol{k})$, which occurs in pair potential models. But even then one can not identify anything in our theory which could be called as $v^{\mathrm{AA}}(\boldsymbol{k})$ or $v^{\mathrm{BB}}(\boldsymbol{k})$ or $v^{\mathrm{AB}}(\boldsymbol{k})$ on their own.

J. B. Pendry (*Imperial College, London, U.K.*). Although CPA is a mean field theory can it be applied to photoemission and transport properties which involve higher-order correlation functions?

B. L. Gyorffy. Yes. The CPA provides a prescription for higher-order averages such as $\langle GG \rangle$ and $\langle GGG \rangle$ without replacing them by products of $\langle G \rangle$. In other words there are CPA vertex corrections. In fact first principles (KKR-CPA) calculations have been done for transport problems photoemission problem and positron annihilation problem, all of which involve such higher-order averages.

N. W. Ashcroft (*Cornell University, U.S.A.*). Evidently, size differences in atoms are being accommodated only insofar as they are manifested in the electronic (band) part of the problem. Yet as one knows from the liquid equivalent of this problem, size differences give rise to a significant entropic component to the overall free energy (i.e. going beyond the (ln C type of term that is being used). This size difference is also important in the known failures of Vegard's Law (most binary systems deviate from this rule). Given this, is it possible to improve on the entropic contributions, as they enter the theory?

B. L. Gyorffy. What I presented is an all electron theory and hence, as a matter of principle, no explicit consideration of atomic size enters the problem. The effect whose liquid state analogue Professor Ashcroft referred to would come into the present discussion if and when the size of the unit cell is allowed to fluctuate as the occupance changes I called these strain fluctuations (they are driven by the Kanzaki forces) and said that for the time being they are not taken into account. Clearly, their contribution to the free energy would have an entropic contribution. However, in the case of the $\mathrm{Pt}_c\mathrm{Ni}_{1-c}$ they would surely favour ordering and therefore would reinforce the ordering tendency we found.

V. Kumar (*Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India*). In the tight-binding model of disordered alloys, effects of local environments could be included reasonably well by treating a configurational average over a cluster of atoms and the single site coherent potential. Has such an attempt been made for KKR-CPA and if so how well does it work?

B. L. Gyorffy. Formally the KKR-CPA is the same as its tight-binding version and new developments can be readily recast into the language of KKR-CPA. The difficulty is the computational implementation. There are a few cluster KKR-CPA studies in the literature (Gonis *et al.* 1983) but not many.

L. M. Falicov (*University of California, Berkeley, U.S.A.*). The CPA is now 24 years old. It was received originally as the alloy theory that could solve all problems in the field. However, no step beyond the single-site (concentration) averaging has been successfully completed yet. Was the optimism misplaced? Is there a chance that the impasse will be overcome?

B. L. Gyorffy. That CPA 24 years ago was for a simple tight-binding model with the uncontrolled parameters and no reference to the thermodynamic state of the nuclei. The theory I presented is a full theory, albeit mean field and single site, of the nuclei and electron system without adjustable parameters. Note that we have successfully calculated the pair correlation functions, $\langle\xi_i\xi_j\rangle-\langle\xi_i\rangle\langle\xi_j\rangle$ for a variety of real systems. Such considerations were not even dreamed of in connection with the CPA in those days. As to the technical questions of whether there is a natural, universally expected approximation which goes beyond the single site CPA the short answer is that there is not. Nevertheless, there are useful recipes like cluster CPA's and direct space methods based on the inverse Monte-Carlo algorithms of significant structure but most of these are as universally accepted as the good old CPA.

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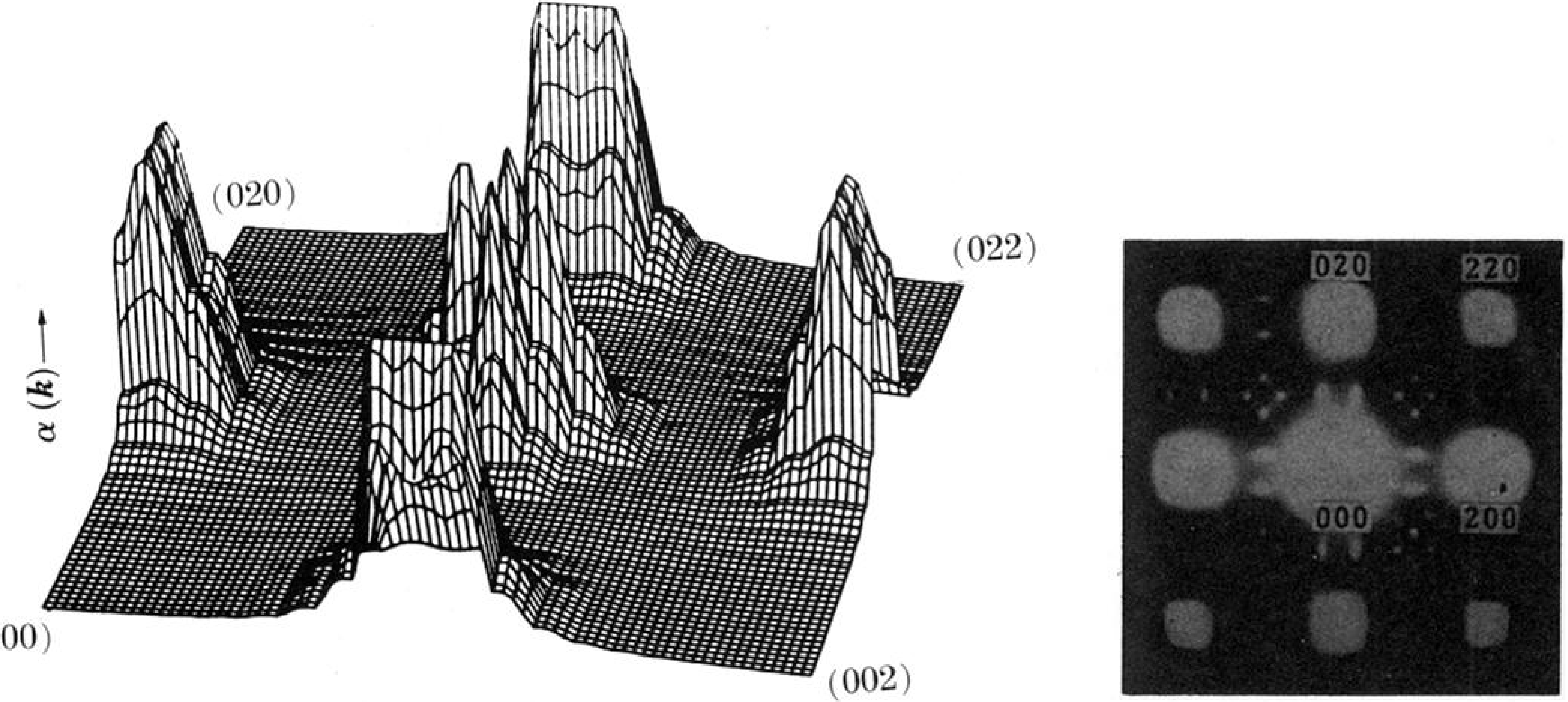

igure 6. The concentration–concentration correlation function $\alpha(\boldsymbol{k})$ (the Warren–Cowley short-nge order parameter) as calculated in the first-principles mean field theory based on the SCF-KKR-PA in the plane containing the reciprocal lattice points 000, 020, 022, 002 for various $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ loys.