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An augmented space approach to the study of random ternary alloys: I. Electronic structure with uncorrelated disorder and short ranged order

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Abstract
We present here a generalized augmented space recursive technique which includes the effects of diagonal and environmental disorder explicitly: an analytic, lattice translational invariant, multiple scattering theory for the study of short range ordering in random ternary alloys. Our generalized augmented space formalism includes atomic correlations over a finite cluster including short range order (SRO). We propose the augmented space recursion (ASR), a computationally fast and accurate technique which incorporates configuration fluctuations over a large local environment. We apply the formalism to a tight-binding linear muffin-tin orbital (LMTO) study of stainless steel $Fe_{80-x}Ni_xCr_{20}$ ($x = 14$ and 17). We have demonstrated the effects of short range ordering by calculating the configuration averaged density of states with and without SRO and with different kinds of cluster environment embedded in an averaged medium.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The search for successful approaches for the study of configuration averaging in disordered systems and ones which go beyond the single-site mean-field approach and include configuration fluctuations about the mean-field has led to four different techniques all of which maintain the essential *Herglotz* analytic properties and lattice translational symmetry of the averaged Green function[3]. They are the augmented space recursion (ASR) [1, 2], the itinerant coherent potential approximation (ICPA) [3], the non-local coherent potential approximation (NL-CPA) [4] and the special quasi-random structures [5]. In a recent paper [6] we have reviewed all four of these methods and have concluded that all four give almost comparable results for the test case of binary Fe_xCr_{1-x} alloys. The first two of these techniques are based on the augmented space theorem (AST) introduced by one of us [7]. The extension of these ideas to situations where disorder is partial or there is short ranged order (SRO), with tendencies to segregate or locally order, have also been proposed [8]. Their successful application to a series of binary alloy systems has been described in great detail in a monograph [2]. However, a larger class of alloys of metallurgical interest involve three constituents.

This paper is an attempt to extend the ASR and its SRO generalization to ternary alloys. The possibility of extension to ternary alloys, indeed to other more complex probability distributions of Hamiltonian parameters, was implicit in the formulation of the augmented space theorem [7]. In this paper we shall look at the ternary distribution in some detail, so that the implications and strengths of the ASR technique become evident.

[3] Herglotz analytic properties include: (i) $\langle\langle G(z)\rangle\rangle$ has singularities only on the real z axis. (ii) The imaginary part of $\mathrm{sgn}[\langle\langle G(z)\rangle\rangle] = -\mathrm{sgn}[z]$ and (iii) $\mathrm{Re}\langle\langle G(z)\rangle\rangle \to 1/E$ as $z = E \to \pm\infty$.

We shall apply our ASR formulation in conjunction with the tight-binding linear muffin-tin orbital (TB-LMTO) minimal basis [10] and combine it with the recursion method of Haydock *et al* [11] to study the electronic structure of the stainless steel alloy $Fe_{66}Ni_{14}Cr_{20}$. Stainless steels are of immediate interest to us, not only because of their commercial interest, but also because extensive experimental work on them has been carried out at our institution [12–15] and we wish to develop a computational technique to analyze the available experimental data.

2. The augmented space formalism for ternary alloys

Since the AST, in particular its formulation for binary alloys, has been described in great detail in many earlier papers, we shall introduce here only those salient points which will be of direct relevance to our generalization to ternary alloys. Interested readers are referred to the review [2] for further details.

The first step is the identification of random variables associated with the effective one electron Hamiltonian of the Kohn–Sham equation derived within the density functional approximation. In our case the randomness is substitutional. There is an underlying crystalline lattice, but the lattice sites are randomly occupied by the constituent atoms. Such randomness may be described by random *occupation variables*. Suppose $\{n_R\}$ be a collection of discrete independent random occupation variables, each associated with a lattice point R. Any physical observable is a function $f(\{n_R\})$ of these random variables.

For a substitutional ternary alloy each random variable n_R takes the values 1, 0 and -1 depending on whether the site labeled by R is occupied by an A, B or C type of atom. For homogeneous, uncorrelated disorder the probabilities for taking these values are proportional to their concentrations: x, y and z. We may decompose the joint probability distribution of these variables as:

$$P(\{n_R\}) = \prod_R p_R(n_R).$$

Each $p_R(n_R)$ is a positive definite function and has finite moments to all orders ($M_n = x + (-1)^n z \leqslant 1\ \forall\ n > 0$). For simple homogeneous disorder the individual probability densities themselves are not labeled by R. In more complex solids, where different sub-lattices may have different kinds of randomness, the probability densities may be labeled by the particular sub-lattice the site R belongs to.

For ternary alloys, each occupation variable can have three possible states $|1\rangle$, $|0\rangle$ and $|\bar{1}\rangle$. These three states span a *configuration space* ϕ_R of rank 3 corresponding to the configurations of the variable n_R. The configuration space of the whole set of variables is then $\Phi = \prod_R^{\otimes} \phi_R$.

The AST now associates with each random variable n_R a self-adjoint operator $N_R \in \phi_R$ such that its eigenvalues are the values randomly taken by n_R and its projected spectral density is the probability density of that variable:

$$\begin{aligned} p_R(n_R) &= x_A\delta(n_R-1) + x_B\delta(n_R) + x_C\delta(n_R+1) \\ &= -\frac{1}{\pi}\lim_{\delta\to 0}\mathrm{Im}\langle \nu_0^R|\left((n_R+\mathrm{i}\delta)I - N_R\right)^{-1}|\nu_0^R\rangle, \end{aligned} \quad (1)$$

where $|\nu_0^R\rangle = \sqrt{x_A}|1\rangle + \sqrt{x_B}|0\rangle + \sqrt{x_C}|\bar{1}\rangle$ is a *state* in ϕ_R. We shall call this the *average* or *reference* state in the configuration space of the site R. Why 'average' state? To understand this we note that $|1\rangle$, $|0\rangle$ and $|\bar{1}\rangle$ are eigenstates of N_R, so that the average of any function $f(n_R)$ is the matrix element of the corresponding operator $\tilde{f}(N_R)$ in this average state:

$$\langle\langle f(n_R)\rangle\rangle = xf(1) + yf(0) + zf(-1) = \langle \nu_0^R|\tilde{f}(N_R)|\nu_0^R\rangle.$$

We define the *average* or *reference* state $|\nu_0\rangle$ in product space Φ of configurations of *all* sites as $|\nu_0\rangle = \prod_R^{\otimes}|\nu_0^R\rangle$. The other two mutually orthogonal states, which together with the *average* state span ϕ_R, represent local configuration fluctuations at the site R about it. If we start with $|\nu_0^R\rangle$ we may generate these other two by a recursive procedure:

$$\begin{aligned} |\nu_{n+1}^R\rangle &= N_R|\nu_n^R\rangle - \alpha_{n+1}|\nu_n^R\rangle - \beta_n^2|\nu_{n-1}^R\rangle \\ & n = 0, 1 \quad \beta_0^2 = 0. \end{aligned}$$

The coefficients α_n and β_n are obtained from the orthogonalization of the basis:

$$\alpha_1 = (x_A - x_C) \qquad \alpha_2 = N_1^2\left[(x_A-x_C)(x_B^2 - 4x_Ax_C)\right]$$

$$\beta_0^2 = 0 \qquad \alpha_3 = \frac{x_B(x_A-x_C)}{-x_A - x_C + (x_A-x_C)^2} \qquad \beta_1^2 = \frac{1}{N_1^2}$$

$$\frac{1}{N_1^2} = (x_A + x_C) - (x_A - x_C)^2$$

$$\begin{aligned} \beta_2^2 &= x_B + \frac{x_B(x_A-x_C)}{(x_A+x_C)-(x_A-x_C)^2} \\ &\times \left[(x_A-x_C) - \frac{x_B(x_A-x_C)}{(x_A+x_C)-(x_A-x_C)^2}\right]. \end{aligned}$$

The other members of the orthonormal basis are:

$$\begin{aligned} |\nu_1^R\rangle &= N_1\left[\sqrt{x_A}(1-x_A+x_C)|1\rangle - \sqrt{x_B}(x_A-x_C)|0\rangle \right.\\ &\quad \left. - \sqrt{x_C}(1+x_A-x_C)|\bar{1}\rangle\right] \\ &= h_1|1\rangle + h_2|0\rangle + h_3|\bar{1}\rangle \\ |\nu_2^R\rangle &= \sqrt{x_A}\left[1 + a - (x_A-x_C)x_BN_1^2\right]|1\rangle + a\sqrt{x_B}|0\rangle + \ldots \\ &\quad + \sqrt{x_C}\left[1 + a + (x_A-x_C)x_BN_1^2\right]|\bar{1}\rangle \\ &= g_1|1\rangle + g_2|0\rangle + g_3|\bar{1}\rangle \end{aligned}$$

with

$$\begin{aligned} a &= (x_A-x_C)^2(x_BN_1^2 - 1) - \frac{1}{N_1^2} \\ \frac{1}{N_2^2} &= x_B\left[(x_A+x_C) - (x_A-x_C)^2x_BN_1^2\right]. \end{aligned} \quad (2)$$

The probability density $p(n_R)$ has a continued fraction expansion:

$$\begin{aligned} p(n_R) &= -\frac{1}{\pi}\lim_{\delta\to 0}\mathrm{Im}\left[\frac{x_A}{z-1} + \frac{x_B}{z} + \frac{x_C}{z-1}\right] \\ &= -\frac{1}{\pi}\lim_{\delta\to 0}\mathrm{Im}\frac{1}{z-\alpha_1 - \frac{\beta_1^2}{z-\alpha_2-\frac{\beta_2^2}{z-\alpha_3}}} \end{aligned}$$

where $z = n_R + \mathrm{i}\delta$.

The representation of the self-adjoint operator N_R in the above basis is a tri-diagonal matrix:

$$\underline{\underline{N}}_R = \begin{pmatrix} \alpha_1 & \beta_1 & 0 \\ \beta_1 & \alpha_2 & \beta_2 \\ 0 & \beta_2 & \alpha_3 \end{pmatrix}.$$

The augmented space theorem [7] states that the configuration average of the function $f(\{n_R\})$ is a matrix element of the operator $\tilde{f}(\tilde{N}_R)$ in the configuration space Φ obtained by replacing each random variable in $f(\{n_R\})$ by its corresponding operators $\{\tilde{N}_R\}$. The matrix element is taken between the *reference* states:

$$\langle\langle f(\{n_R\})\rangle\rangle = \langle \nu_0|\tilde{f}(\{\tilde{N}^{(R)}\})|\nu_0\rangle, \tag{3}$$

where

$$\tilde{N}^{(R)} = I \otimes I \otimes \cdots N_R \otimes \cdots \otimes I \otimes \cdots.$$

The operator $\tilde{N}_R$ in the basis described above, is given by [9]:

$$\begin{aligned} N_R &= \alpha_1\mathcal{P}_R^0 + \alpha_2\mathcal{P}_R^1 + \alpha_3\mathcal{P}_R^2 + \beta_1\mathcal{T}_R^{01} + \beta_2\mathcal{T}_R^{12} \\ \tilde{N}^{(R)} &= \alpha_1\tilde{\mathcal{P}}_R^0 + \alpha_2\tilde{\mathcal{P}}_R^1 + \alpha_3\tilde{\mathcal{P}}_R^2 + \beta_1\tilde{\mathcal{T}}_R^{01} + \beta_2\tilde{\mathcal{T}}_R^{12}. \end{aligned} \tag{4}$$

We shall denote the *average* state $|\nu_0\rangle \equiv \prod_R^{\otimes} |\{\nu_0^R\}\rangle$ with the notation $|\{\emptyset\}\rangle$. Any other configuration state is labeled by its *cardinality sequence*:

$$|\{\mathcal{C}_1\} \equiv \{R_i\},$$

$$\{\mathcal{C}_2\} \equiv \{R_j\}\rangle = \prod_{\{R_i\}} |\nu_1^{R_i}\rangle \otimes \prod_{\{R_j\}} |\nu_2^{R_j}\rangle \otimes \prod_{R\neq\{R_i\}\oplus\{R_j\}} |\nu_0^R\rangle.$$

The configuration states $|\{\mathcal{C}_1\},\{\mathcal{C}_2\}\rangle$ span the full configuration space $\Phi = \prod^{\otimes}\phi_R$.

Here, $\tilde{\mathcal{P}}_R^j = I \otimes \ldots P_R^j \otimes \cdots (j = 0,1,2)$ are the projection operators with $P_R^j = |j_R\rangle\langle j_R|$ and $\tilde{\mathcal{T}}_R^{jj'} = I \otimes \cdots T_R^{jj'} \otimes \cdots (j \neq j' = 0,1,2)$ are the transfer operators with $T_R^{jj'} = (|j_R\rangle\langle j'_R| + |j'_R\rangle\langle j_R|)$ in the configuration space Φ. $\tilde{\mathcal{T}}_R^{01}$ either creates a configuration fluctuation at R in the 'average' state or destroys one from the state with one fluctuation, $\tilde{\mathcal{T}}_R^{12}$ creates a fluctuation at R in the state with one fluctuation or destroys a fluctuation, at R, in a state with two and $\tilde{\mathcal{T}}_R^{02}$ creates two fluctuations at R in the average state or destroys two, at R, in the state with two fluctuations.

Unlike the corresponding operator for binary randomness, N_R is not idempotent i.e. $M_R = N_R^2 \neq N_R$. The representation of M_R in the same basis is:

$$M_R = \begin{pmatrix} A_1 & B_{12} & B_{13} \\ B_{12} & A_2 & B_{23} \\ B_{13} & B_{23} & A_3 \end{pmatrix} \tag{5}$$

with

$$A_1 = \alpha_1^2 + \beta_1^2, \qquad A_2 = \alpha_2^2 + \beta_1^2 + \beta_2^2$$

$$A_3 = \alpha_3^2 + \beta_2^2 \qquad B_{12} = (\alpha_1 + \alpha_2)\beta_1$$

$$B_{13} = \beta_1\beta_2 \qquad B_{23} = (\alpha_3 + \alpha_2)\beta_2.$$

The operator $\tilde{M}_R$ in the basis chosen then becomes:

$$\tilde{M}_R = A_1\tilde{\mathcal{P}}_R^0 + A_2\tilde{\mathcal{P}}_R^1 + A_3\tilde{\mathcal{P}}_R^2 + B_{12}\tilde{\mathcal{T}}_R^{01} + B_{13}\tilde{\mathcal{T}}_R^{02} + B_{23}\tilde{\mathcal{T}}_R^{12}.$$

Any random local potential parameter X_R now can be expressed in terms of n_R as:

$$X_R = \tfrac{1}{2}n_R(1+n_R)X_{\mathrm{A}} + (1-n_R)(1+n_R)X_{\mathrm{B}} + \tfrac{1}{2}n_R(n_R-1)X_{\mathrm{C}} \tag{6}$$

where X_{A}, X_{B}, X_{C} are the values taken by X_R corresponding to the random variable n_R having the value $1, 0, -1$ respectively. Replacing n_R by the corresponding operator N_R, and n_R^2 by M_R, X_R is replaced by an operator $\tilde{X}_R$ in the 'configuration' space spanned by the 'configuration' states of N_R and can be written as:

$$\begin{aligned} \tilde{X}_R &= \tfrac{1}{2}(\tilde{M}_R + \tilde{N}_R)X_{\mathrm{A}} + (\tilde{I} - \tilde{M}_R)X_{\mathrm{B}} + \tfrac{1}{2}(\tilde{M}_R - \tilde{N}_R)X_{\mathrm{C}} \\ &= X_1\tilde{\mathcal{I}} + X_2\tilde{\mathcal{P}}_R^0 + X_3\tilde{\mathcal{P}}_R^1 + X_4\tilde{\mathcal{P}}_R^2 + X_5\tilde{\mathcal{T}}_R^{01} \\ &\quad + X_6\tilde{\mathcal{T}}_R^{12} + X_7\tilde{\mathcal{T}}_R^{02} \end{aligned} \tag{7}$$

here

$$X_1 = X_{\mathrm{B}}$$

$$X_2 = \tfrac{1}{2}[\alpha_1(X_{\mathrm{A}} - X_{\mathrm{C}}) + (X_{\mathrm{A}} - 2X_{\mathrm{B}} + X_{\mathrm{C}})A_1]$$

$$X_3 = \tfrac{1}{2}[\alpha_2(X_{\mathrm{A}} - X_{\mathrm{C}}) + (X_{\mathrm{A}} - 2X_{\mathrm{B}} + X_{\mathrm{C}})A_2]$$

$$X_4 = \tfrac{1}{2}[\alpha_3(X_{\mathrm{A}} - X_{\mathrm{C}}) + (X_{\mathrm{A}} - 2X_{\mathrm{B}} + X_{\mathrm{C}})A_3]$$

$$X_5 = \tfrac{1}{2}[\beta_1(X_{\mathrm{A}} - X_{\mathrm{C}}) + (X_{\mathrm{A}} - 2X_{\mathrm{B}} + X_{\mathrm{C}})B_{12}]$$

$$X_6 = \tfrac{1}{2}[(X_{\mathrm{A}} - 2X_{\mathrm{B}} + X_{\mathrm{C}})B_{13}]$$

$$X_7 = \tfrac{1}{2}[\beta_2(X_{\mathrm{A}} - X_{\mathrm{C}}) + (X_{\mathrm{A}} - 2X_{\mathrm{B}} + X_{\mathrm{C}})B_{23}].$$

The projection operators essentially count the number of configuration fluctuations locally at sites R and the transfer operators create or annihilate configuration fluctuations, again *locally*.

For solution of the Kohn–Sham equations we shall use the representation of the effective density functional (DFT) Hamiltonian in the TB-LMTO basis. The TB-LMTO basis is appropriate for us since it leads to a sparse Hamiltonian representation and we shall use the recursion method of Haydock [11] to calculate the Green function. The equation (7) gives us a prescription of how to set up the augmented space operators corresponding to the random *local* potential parameters E_L^ν, C_{RL}, $\Delta_{RL}^{1/2}$ and o_{RL}. The second order Hamiltonian has the form:

$$\begin{aligned} \tilde{H} &= \tilde{E}^\nu + \tilde{h} - \tilde{h}\tilde{o}\tilde{h} \\ \tilde{h} &= \sum_R \left(\underline{\underline{\tilde{C}}}_R - \underline{\underline{\tilde{E}}}^\nu\right) \otimes \mathcal{P}_R + \sum_{R,R'} \left(\underline{\underline{\tilde{\Delta}}}_R^{1/2} \underline{\underline{\tilde{S}}}_{R,R'} \underline{\underline{\tilde{\Delta}}}_{R'}^{1/2}\right) \otimes \mathcal{T}_{RR'} \\ \tilde{o} &= \sum_R \underline{\underline{\tilde{o}}}_R \otimes \mathcal{P}_R \end{aligned} \tag{8}$$

where the matrix operators are matrices in angular momentum space labeled by L, which is the composite index $(\ell m\sigma)$. $\mathcal{P}_R$ and $\mathcal{T}_{RR'}$ are projection and transfer operators respectively in the Hilbert space $\mathcal{H}$ spanned by the 'tight-binding' basis $\{|R\rangle\}$. $\tilde{C}_{RL}$, $\tilde{E}^{\nu}_{L}$, $\tilde{o}_{RL}$ and $\tilde{\Delta}^{1/2}_{RL}$ are operators in the configuration space of n_R and have the same form as $\tilde{X}_R$ described above. The Hamiltonian is a function of a whole set of random variables $\{n_R\}$, one for each site. Usually the structure matrix $S_{RL,R'L'}$ is not random and $\tilde{S}_{RL,R'L'} = \langle\langle S_{RL,R'L'}\rangle\rangle I$. However, if the atomic size differences between the three constituents are large there can be significant local lattice distortions which lead to off-diagonal disorder in the structure matrix.

In such a situation, the diagonal term of the structure matrix can be expressed as:

$$S_{RL,RL} = \frac{n_R(n_R+1)}{2} S^{AA}_{RL,RL} + (1-n_R^2) S^{BB}_{RL,RL} + \frac{n_R(n_R-1)}{2} S^{CC}_{RL,RL} \tag{9}$$

and the off-diagonal term as:

$$\begin{aligned} S_{RL,R'L'} = {} & \frac{n_R n_{R'}(n_R+1)(n_{R'}+1)}{4} S^{AA}_{RL.R'L'} \\ & + (1-n_R^2)(1-n_{R'}^2) S^{BB}_{RL,R'L'} \cdots \\ & \cdots + \frac{n_R n_{R'}(n_R-1)(n_{R'}-1)}{4} S^{CC}_{RL,R'L'} \cdots \\ & \cdots + \left[\frac{n_R(n_R+1)(1-n_{R'}^2)}{2} \right. \\ & \left. + \frac{n_{R'}(1-n_R^2)(n_{R'}+1)}{2}\right] S^{AB}_{RL.R'L'} \cdots \\ & \cdots + \frac{n_R n_{R'}}{4}\left[(n_R+1)(n_{R'}-1) \right. \\ & \left. + (n_R-1)(n_{R'}+1)\right] S^{AC}_{RL.R'L'} \cdots \\ & \cdots + \left[\frac{(1-n_R^2)(n_{R'}-1)}{2} n_{R'} \right. \\ & \left. + \frac{(n_R-1)(1-n_{R'}^2)}{2} n_R\right] S^{BC}_{RL,R'L'}. \end{aligned} \tag{10}$$

Replacing n_R by the corresponding operator $\tilde{N}_R$ and n_R^2 by $\tilde{M}_R$, we get for the lattice space diagonal term:

$$\tilde{S}_{RL,RL} = S^{BB}_{RL,RL}\tilde{\mathcal{I}} + S^{(1)}_{RL,RL}\tilde{M}_R + S^{(2)}_{RL,RL}\tilde{N}_R. \tag{11}$$

These operators either count or create/annihilate configuration fluctuations locally at sites R. For the off-diagonal terms we get:

$$\begin{aligned} \tilde{S}_{RL,R'L'} = {} & S^{BB}_{RL,R'L'}\tilde{I} + S^{(3)}_{RL,R'L'}(\tilde{M}_R + \tilde{M}_{R'}) \\ & + S^{(4)}_{RL,R'L'}(\tilde{N}_R + \tilde{N}_{R'}) + \cdots \\ & \cdots S^{(5)}_{RL,R'L'}\tilde{M}_R \otimes \tilde{M}_{R'} + S^{(6)}_{RL,R'L'}(\tilde{M}_R \otimes \tilde{N}_{R'} \\ & + \tilde{N}_R \otimes \tilde{M}_{R'}) + S^{(7)}_{RL,R'L'}\tilde{N}_R \otimes \tilde{N}_{R'} \end{aligned} \tag{12}$$

where

$$\begin{aligned} S^{(1)}_{RL,R'L'} &= \tfrac{1}{2}(S^{AA}_{RL,R'L'} + S^{CC}_{RL,R'L'} - 2S^{BB}_{RL,R'L'}) \\ S^{(2)}_{RL,R'L'} &= \tfrac{1}{2}(S^{AA}_{RL,R'L'} - S^{CC}_{RL,R'L'}) \\ S^{(3)}_{RL,R'L'} &= \tfrac{1}{2}(S^{AB}_{RL,R'L'} + S^{BC}_{RL,R'L'} - 2S^{BB}_{RL,R'L'}) \\ S^{(4)}_{RL,R'L'} &= \tfrac{1}{2}(S^{AB}_{RL,R'L'} - S^{CB}_{RL,R'L'}) \\ S^{(5)}_{RL,R'L'} &= \tfrac{1}{4}(S^{AA}_{RL,R'L'} + 4S^{BB}_{RL,R'L'} + S^{CC}_{RL,R'L'} \\ &\quad - 4S^{AB}_{RL,R'L'} + 2S^{AC}_{RL,R'L'} - 4S^{BC}_{RL,R'L'}) \\ S^{(6)}_{RL,R'L'} &= \tfrac{1}{4}(S^{AA}_{RL,R'L'} - S^{CC}_{RL,R'L'} - 2S^{AB}_{RL,R'L'} + 2S^{BC}_{RL,R'L'}) \\ S^{(7)}_{RL,R'L'} &= \tfrac{1}{4}(S^{AA}_{RL,R'L'} + S^{CC}_{RL,R'L'} - 2S^{AC}_{RL,R'L'}). \end{aligned} \tag{13}$$

It is easy to check that all the factors above vanish when the structure matrices are independent of site occupation (i.e. not random). The operators in the first two lines of equation (12) either count or create/annihilate configuration fluctuations at either of the two sites R and R'. The last four operators in the third and fourth lines of equation (12) either count or create/annihilate configuration fluctuations *simultaneously* at both the sites R and R'. These operators are essentially *non-local* and cannot be dealt with in a local (single-site) mean-field approximation. The augmented Hamiltonian $\tilde{H}$ is an operator in the augmented space $\Psi = \mathcal{H} \otimes \Phi$.

The augmented space theorem [7] tells us:

$$\langle\langle f[H(\{n_R\})]\rangle\rangle = \langle\{\emptyset\}|f[\tilde{H}(\{\tilde{N}_R, \tilde{M}_R\})]|\{\emptyset\}\rangle. \tag{14}$$

We may now combine the above with the recursion method of Haydock *et al* [11] and obtain the configuration averaged Green function as a continued fraction using the same technique as for binary alloys [6].

$$\begin{aligned} \langle\langle G_{RL,RL}(z)\rangle\rangle &= \langle RL \otimes \{\emptyset\}|(z\tilde{I} - \tilde{H})^{-1}|RL \otimes \{\emptyset\}\rangle \\ &= \cfrac{1}{z - a_1 - \cfrac{b_1^2}{z - a_2 - \cfrac{b_2^2}{z - a_3 - \cfrac{b_3^2}{\ddots\, z - a_N - T(z)}}}}. \end{aligned} \tag{15}$$

The terminator $T(z)$ is estimated from the initial coefficients $\{a_n, b_n\}$, $1 \leqslant n \leqslant N-1$ using the ideas of Beer and Pettifor [16]. The density of states *per atom* is then obtained from

$$\begin{aligned} \langle\langle n(E)\rangle\rangle &= \lim_{\delta\to 0}\left[-\frac{1}{N\pi}\sum_{RL} \mathrm{Im}\langle\langle G_{RL,RL}(E + \mathrm{i}\delta)\rangle\rangle\right] \\ &= \lim_{\delta\to 0}\left[-\frac{1}{\pi}\sum_{L} \mathrm{Im}\langle\langle G_{RL,RL}(E + \mathrm{i}\delta)\rangle\rangle\right]. \end{aligned}$$

The second line follows only if the disorder is *homogeneous* and the averaged Green function is lattice translation invariant or independent of the R index.

The local charge densities in atomic spheres around specific atom types $\rho^{A}(\vec{r})$, $\rho^{B}(\vec{r})$ and $\rho^{C}(\vec{r})$ are obtained from the energy moments of atom-projected densities of states $n^{A}(E)$, $n^{B}(E)$ and $n^{C}(E)$. These are obtained as described above, except for the Hamiltonians similar to (7) but with potential parameters $\tilde{C}_{R'L}$ and $\tilde{\Delta}^{1/2}_{R'L}$ being the same as before unless $R' = R$ when they are C^{A}_{RL}, C^{B}_{RL} or C^{C}_{RL} and $\Delta^{1/2\mathrm{A}}_{RL}$, $\Delta^{1/2\mathrm{B}}_{RL}$ or $\Delta^{1/2\mathrm{C}}_{RL}$. These local charge densities are inputs into the density functional self-consistency loop, which then produces the self-consistent potential parameters, starting from the pure atomic potential parameters to those of the atom immersed in the disordered alloy. The Madelung energy is obtained according to the prescription given by Ruban and Skriver [17].

2.1. Augmented space formalism with SRO

Let us now turn to a problem in which the variables $\{n_R\}$ are correlated. Mookerjee and Prasad [8] have proposed a formulation based on the augmented space technique which takes into account correlated disorder in binary alloys. We shall now propose a generalization to ternary alloys. If we choose any site R_0 and suppose that n_{R_0} is correlated with the neighboring $\{n_{R_k}\}$ $k = 1, 2, \ldots, p$, then the joint probability distribution of all the variables can be expanded as

$$P(n_{R_0}, n_{R_1}, \ldots, n_{R_p}, n_{R_{p+1}}, \ldots) = p(n_{R_0}) \prod_{k=1}^{p} p(n_{R_k}|n_{R_0}, \ldots n_{R_{k-1}}) \prod_{k>p}^{\infty} p(n_{R_k}) \cdots.$$

Note that if the SRO is itself homogeneous, it is immaterial which site we choose as R_0. Lattice translational symmetry is still valid in the full augmented space $\Psi = \mathcal{H} \otimes \Phi$, where $\mathcal{H}$ is the Hilbert space spanned by the basis $|R\rangle$. This is schematically shown in figure 1.

The representation of the operator associated with the random variable n_{R_0} corresponding to the probability density $p(n_{R_0})$ is given by equation (4).

Let us now come to the variables $n_{R_k}, k = 1, 2, \ldots, p$ which are correlated to n_{R_0} but not to one another. We now have to deal with the conditional probability densities depending on the value taken by the variable n_{R_0}. For each such value taken by n_{R_0}, we associate the corresponding conditional probability density $p(n_{R_k}|n_{R_0} = j)$, where $j = 0, 1$ or 2. Since the conditional probability densities are also positive definite and assumed to have finite moments to all orders, we may associate with them operators $N^{(j)}_{R_k}$ such that

$$p(n_{R_k}|n_{R_0} = j) = -\frac{1}{\pi} \lim_{\delta \to 0} \mathrm{Im} \langle \nu_0^{R_k} | \left((n_{R_k} + \mathrm{i}\delta) I - N^{(j)}_{R_k} \right)^{-1} | \nu_0^{R_k} \rangle.$$

The operator $\tilde{N}_{(R_k)}$ we wish to associate with the variable n_{R_k} should be that $M^{(j)}_{R_k}$ which corresponds to the particular configuration j which n_{R_0} takes. A natural generalization then takes the form

$$\tilde{N}_{R_k} = \sum_j P^{(j)}_{R_0} \otimes N^{(j)}_{R_k} \otimes I \otimes I \otimes \cdots \tag{16}$$

where $P^{(j)}_{R_0}$ are the projection operators which project onto the eigenstates $|j\rangle$ of M_{R_0}.

The operators associated with all further sites R_{p+1} are the same as equation (4), as they are uncorrelated with R_0. The basic augmented space theorem still holds good rigorously, but $\tilde{N}_{R_k}$, instead of being of the form given by equation (4), now has the form given by equation (16). For electronic structure calculations in a disordered system, f is chosen to be the matrix element of the Green function $(zI - H)^{-1}$, where H describes the random Hamiltonian of the system and n_R are the site occupation variables.

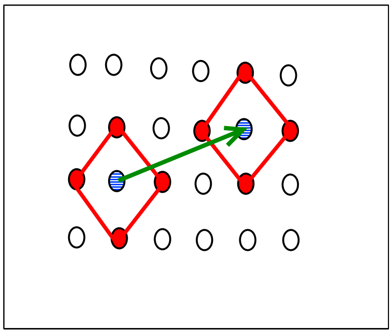

Figure 1. The translational symmetry for homogeneous SRO. The plaquettes shown have correlated site occupation.

The construction of different operators in augmented space associated with the site occupation variables for correlated disorder in binary alloys has already been discussed in detail by Mookerjee and Prasad [8]. Here and in the following we shall derive a similar theory of correlated disorder for random ternary alloys which is not a trivial generalization of the previous theory.

For a ternary alloy the SRO is described by three distinct Warren–Cowley parameters α^{AB}, α^{BC} and α^{AC} which describe pair correlations between occupations of the three distinct pairs of components. If $P^{\lambda\lambda'}$ is the probability of the central site R_0 being occupied by a λ type atom and the site R_k being occupied by a λ' type atom, then by definition:

$$P^{\mathrm{AB}} = x_{\mathrm{B}}(1 - \alpha^{\mathrm{AB}}) \qquad P^{\mathrm{AC}} = x_{\mathrm{C}}(1 - \alpha^{\mathrm{AC}})$$

$$P^{\mathrm{AA}} = 1 - (P^{\mathrm{AB}} + P^{\mathrm{AC}}) = (x_{\mathrm{A}} + x_{\mathrm{B}}\alpha^{\mathrm{AB}} + x_{\mathrm{C}}\alpha^{\mathrm{AC}})$$

where $x_{\mathrm{A}} + x_{\mathrm{B}} + x_{\mathrm{C}} = 1$.

The conditional probability densities $p(n_{R_k}|n_{R_0} = j)$ $(j = 1, 0, -1)$ associated with the sites belonging to the first nearest neighbor shell can be expressed in terms of the Warren–Cowley SRO parameters as

$$p(n_{R_k}|n_{R_0} = j) = X^{(j)}_{\mathrm{A}} \delta(n_{R_k} - 1) + X^{(j)}_{\mathrm{B}} \delta(n_{R_k}) + X^{(j)}_{\mathrm{C}} \delta(n_{R_2} + 1) \tag{17}$$

where

$$X^{(1)}_{\mathrm{A}} = x_{\mathrm{A}} + (x_{\mathrm{B}}\alpha_{\mathrm{AB}} + x_{\mathrm{C}}\alpha_{\mathrm{AC}}) \qquad X^{(1)}_{\mathrm{B}} = x_{\mathrm{B}}(1 - \alpha_{\mathrm{AB}})$$

$$X^{(i)}_{\mathrm{C}} = x_{\mathrm{C}}(1 - \alpha_{\mathrm{AC}}) \qquad X^{(0)}_{\mathrm{A}} = x_{\mathrm{A}}(1 - \alpha_{\mathrm{AB}})$$

$$X^{(0)}_{\mathrm{B}} = x_{\mathrm{B}} + (x_{\mathrm{A}}\alpha_{\mathrm{AB}} + x_{\mathrm{C}}\alpha_{\mathrm{BC}}) \qquad X^{(0)}_{\mathrm{C}} = x_{\mathrm{C}}(1 - \alpha_{\mathrm{BC}})$$

$$X^{(\bar{1})}_{\mathrm{A}} = x_{\mathrm{A}}(1 - \alpha_{\mathrm{AC}}) \qquad X^{(\bar{1})}_{\mathrm{B}} = x_{\mathrm{B}}(1 - \alpha_{\mathrm{BC}})$$

$$X^{(\bar{1})}_{\mathrm{C}} = x_{\mathrm{C}} + (x_{\mathrm{A}}\alpha_{\mathrm{AC}} + x_{\mathrm{B}}\alpha_{\mathrm{BC}}).$$

When there is no SRO i.e. $\alpha_{AB} = \alpha_{BC} = \alpha_{AC} = 0$, the conditional probabilities of the second variable n_{R_k} become identical to the unrestricted probability density of the variable n_{R_0}. Since we have chosen to include conditional probabilities which incorporate pairwise correlations alone, these are the only correlation coefficients in the model. Three site correlations would have required further such parameters: $\alpha_{(A,BC)}$, $\alpha_{(B,AC)}$, $\alpha_{(C,AB)}$ and $\alpha_{(ABC)}$. These we have ignored in our present model.

The representation of the conditional operators are (compare with equation (4)):

$$N^{(j)}_{R_k} = a^{(j)}_1 \mathcal{P}^0_{R_k} + a^{(j)}_2 \mathcal{P}^1_{R_k} + a^{(j)}_3 \mathcal{P}^2_{R_k} + b^{(j)}_1 \mathcal{T}^{01}_{R_k} + b^{(j)}_2 \mathcal{T}^{12}_{R_k} \quad (18)$$

where

$$a^{(j)}_1 = (X^{(j)}_A - X^{(j)}_C);$$

$$b^{(j)2}_1 = (X^{(j)}_A + X^{(j)}_C) - (X^{(j)}_A - X^{(j)}_C)^2;$$

$$a^{(j)}_2 = \frac{a^{(j)}_1 X^{(j)}_B}{b^{(j)2}_1 - a^{(j)}_1} \qquad b^{(j)2}_2 = X^{(j)}_B - \frac{X^{(j)}_B\, a^{(j)}_2 a^{(j)}_3}{b^{(j)2}_1};$$

$$a^{(j)}_3 = -a^{(j)}_2 - a^{(j)}_1.$$

In equation (16) we also require representations of the projection operators $P^{(j)}_{R_0}$. The representation of these operators in the basis of eigenfunctions of $\tilde{N}_{R_0}$ are very simple:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

However, all our representations so far have been in the basis in which M_{R_0} was tri-diagonal. This basis $|\nu^{R_0}_0\rangle$, $|\nu^{R_0}_1\rangle$ and $|\nu^{R_0}_2\rangle$ may be generated by a recursion, as described before. We refer back to the generation of the orthogonal basis in ϕ_R and obtain the orthogonal transformation matrix between the eigenstates of M_{R_0} and the basis in which that operator is tri-diagonal:

$$\begin{pmatrix} |\nu_0\rangle \\ |\nu_1\rangle \\ |\nu_2\rangle \end{pmatrix} = U \begin{pmatrix} |1\rangle \\ |0\rangle \\ |\bar{1}\rangle \end{pmatrix} \qquad U = \begin{pmatrix} \sqrt{x_A} & \sqrt{x_B} & \sqrt{x_C} \\ h_1 & h_2 & h_3 \\ g_1 & g_2 & g_3 \end{pmatrix}.$$

Thus any operator Q whose representation in the basis of eigenfunctions is known can be transformed to the other basis via: $Q' = U^\dagger \cdot Q \cdot U$

The representations of the projection operators in this new basis are then:

$$P^{(1)}_{R_0} = \begin{pmatrix} x_A & \sqrt{x_A x_B} & \sqrt{x_A x_C} \\ \sqrt{x_A x_B} & x_B & \sqrt{x_B x_C} \\ \sqrt{x_A x_C} & \sqrt{x_B x_C} & x_C \end{pmatrix}$$

$$P^{(0)}_{R_0} = \begin{pmatrix} h_1^2 & h_1 h_2 & h_1 h_3 \\ h_1 h_2 & h_2^2 & h_2 h_3 \\ h_1 h_3 & h_2 h_3 & h_3^2 \end{pmatrix}$$

and

$$P^{(\bar{1})}_{R_0} = \begin{pmatrix} g_1^2 & g_1 g_2 & g_1 g_3 \\ g_1 g_2 & g_2^2 & g_2 g_3 \\ g_1 g_3 & g_2 g_3 & g_3^2 \end{pmatrix}.$$

Explicit expressions for the operators $\tilde{N}_{(R_k)}$ are given in the appendix. Unlike the operators for the case without SRO, which creates or annihilates a configuration fluctuation only at the site R_k, now the generalized operator not only creates or annihilates a configuration fluctuation at the site R_k, but also one at the correlated site R_0. In addition it also creates or annihilates two configuration fluctuations simultaneously at the sites R_k and R_0. In this sense, SRO introduces off-diagonal disorder, which single-site mean-field approaches cannot take care of without further approximations.

3. Results and discussion

The first application of the formalism developed in section 2 will be to the stainless steel alloy $Fe_{66}Ni_{14}Cr_{20}$. The upper panels of figure 2 show the atom-projected density of states of stainless steel (left) and the total density of states (right), which is their concentration weighted sum. The alloy is in a face-centered cubic structure and the lattice constant is taken to be that at which the total energy is a minimum. The lower panel shows the density of states of pure Fe, Ni and Cr in the same face-centered cubic lattice as the alloy and with the same lattice constant (left) and their concentration weighted sum (right). The lower panels are shown in order to compare these densities of states with those for the fully disordered alloy, in order to analyze the results. We note the following features:

(i) The energy spectra of Fe and Ni have considerable overlap, while both have much smaller overlap with the spectrum of Cr. FeCr and NiCr form 'split band' alloys, while FeNi structures overlap and hybridize considerably. The ternary alloy should show all these features.

(ii) The main structure in the density of states of the alloy has its origin in those of the individual constituents Fe, Ni and Cr.

(iii) It is known that alloying non-iso-electronic constituents lead to charge transfer between them. One of the consequences of charge transfer is the shifting of band centers. Comparison between the left and right panels shows that the Cr spectrum is pushed to higher energies, while those of Fe and Ni are pushed lower.

(iv) One of the main effects of disorder induced scattering of Bloch-like electron states in ordered systems is the smoothing out of the sharp structures in the density of states. This 'smoothing' is the result of the imaginary part of the self-energy which arises because of scattering by configuration fluctuations. Such smooth structures are evident in our results. The real part of the self-energy leads to the shifting of the energy spectrum, described in section 2. However, the self-energy is sufficiently small so that the main structures of the partial (atom-projected) density of states are preserved.

The effect of composition variation of the alloy on the densities of states is shown in figure 3. Here we show the partial (atom-projected) and total densities of states for two other alloy compositions: $Fe_{0.05}Ni_{0.05}Cr_{0.99}$ and $Fe_{0.99}Ni_{0.05}Cr_{0.05}$. In the case (shown in the top panel of figure 3) where Fe and Ni are almost dilute impurities in

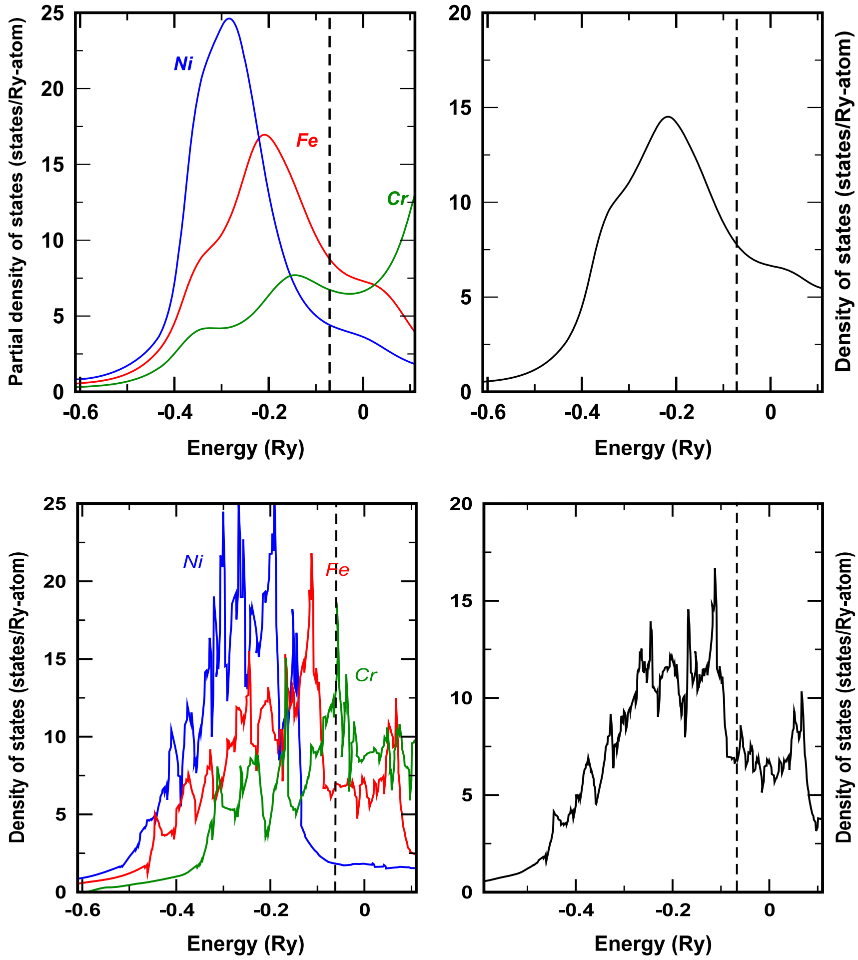

Figure 2. Top panel: the atom-projected or partial (left) and total (right) densities of states of the $Fe_{66}Ni_{14}Cr_{20}$ alloy. The color scheme is as follows: the red curve stands for Fe-projected, blue curve for Ni-projected, green curve for Cr-projected and the black curve for total density of states of the alloy. The vertical dashed line marks the position of the Fermi level (E_F). Bottom panel: the densities of states of pure Ni, Fe and Cr superposed on one another (left) and their concentration weighted average (right).

Cr, their densities of states are narrower than stainless steel composition. This is characteristic of impurity like bands in a nearly split band situation. When Fe is the main constituent and Ni and Cr are in dilution, the hybridization between the bands arising out of the constituents is much stronger and the partial density of states is much smoother than in the previous example.

The next application is to study the effect of short ranged order on the electronic structure of stainless steel. We shall use our pairwise correlated model. The accompanying table 1 explains the consequences of specific triads of values of the three Warren–Cowley parameters.

We have chosen a few specific examples, where the physical interpretation is simple. For example, the first choice is $\alpha_{AB} = 1, \alpha_{AC} = 1$ and $\alpha_{BC} = 0$. Here, in the alloy A atoms do not like to sit next to either B or C atoms. The alloying between B and C is, on the other hand, random without any tendency either to segregate or order. In this alloy, then, the A component tends to segregate out of the perfectly random BC alloy component. In the leftmost frame of the top row of figure 4 we show the density of states for this example. Next to it, for comparison, we show the density of states of pure Fe (in a face-centered cubic lattice with the same lattice constant as the ternary alloy) and that of ordered NiCr, again in a face-centered cubic lattice with the same lattice constant as the ternary alloy. This ordered alloy is equi-atomic and hence in an L10 configuration. The comparison clearly indicates the origin of the two peaked structures in the configuration averaged density of states. The higher peak around −0.2 Ryd arises out of contributions both

Table 1. Specific cases of Warren–Cowley parameters and their interpretation.

α_{AB}	α_{AC}	α_{BC}	Type of correlation	Example
1	1	0	BC alloyed, A segregated	NiCr–Fe
1	0	1	AC alloyed, B segregated	FeCr–Ni
0	1	1	AB alloyed, C segregated	FeCr–Cr
1	0	0	*AC*, BC alloyed but pairwise segregated	FeCr–NiCr
0	1	0	AB, BC alloyed but pairwise segregated	FeNi–NiCr
0	0	1	AB, AC alloyed but pairwise segregated	FeNi–FeCr
1	1	1	A, B, C all segregated	Fe–Ni–Cr

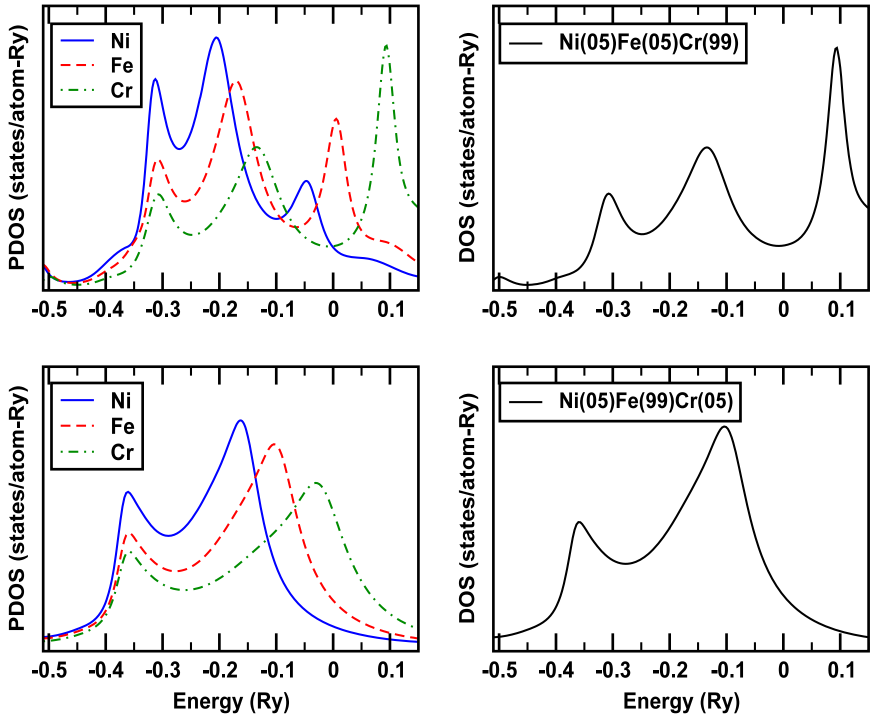

Figure 3. Top panel (left): the partial or atom-projected densities of states for the $Fe_{0.05}Ni_{0.05}Cr_{0.99}$ disordered alloy. Top panel (right): the total density of states for $Fe_{0.05}Ni_{0.05}Cr_{0.99}$. Bottom panel: the same as shown for $Fe_{0.99}Ni_{0.05}Cr_{0.05}$.

from segregated Fe and the Ni partial density of states of the NiCr alloy, while the peak around 0.2 Ryd comes from the Cr partial density of the NiCr alloy. We see both the structure shifting due to charge transfer on alloying and broadening due to scattering by configuration fluctuations. The next frame on the top row shows the situation where B (Ni) segregates from a random AC (FeCr) binary component. The structure is now rather different, with a two peaked structure with equal weights arising out of the FeCr alloy and a lower energy structure around -0.4 Ryd arising out of the segregated Ni component. This Ni structure showed up as a shoulder around -0.4 Ryd in the first example as well, however here it is more prominent. This is because the structure of a segregated Ni atom sitting in an FeCr environment is much more pronounced than the equivalent structure in an NiCr alloy.

At a first glance most of the densities of states shown in figure 4 appear to be of two specific types. Their differences in structure are not immediately visually apparent. A more subtle analysis of these differences is through the energy moment functions of the densities of states:

$$M_n(E) = \int_{-\infty}^{E} \mathrm{d}E'\, E'^n n(E').$$

The second moment ($n = 2$) tells us how spread out the density of states is about its mean value. The fourth moment ($n = 4$) tells us about the kurtosis of the energy distribution. These characteristics are standard in the analysis of the shapes of distribution functions and help to carefully distinguish between almost similar shapes. It will be interesting to note that the analysis of the 'convergence' of the recursion method which is linked to the convergence of the shape of the density of states is also related to the convergence of these moment functions (Haydock [18]). These energy moment functions are shown in figure 5.

We note that the second moment functions are arranged as follows $M_2(110) < M_2(101) < M_2(011)$. This reflects the fact that for example, the lowest moment is for Fe segregated from an NiCr random alloy. The main spread comes from the NiCr structure. Segregated Fe has states which hybridize with that of the Ni partial density in NiCr, producing simply a shoulder in the structure. The next higher moment occurs for Ni segregated from a random FeCr alloy. The segregated Ni states are rather more separated from the two peaked FeCr structure, producing a much more pronounced 'impurity' structure at around -0.4 Ryd. This three peaked structure has a larger energy spread. Finally the highest moment in this series is for Cr segregated in a FeNi alloy. Fe and Ni bands overlap considerably, whereas Cr bands are split from the FeNi ones. Segregated Cr states then form sharp 'impurity' structures which make the spread for this example the highest. Second moments for the other examples can be discussed similarly. Here $M_2(100) < M_2(010) < M_2(001)$.

The fourth moment measures kurtosis or the sharper than Gaussian 'localization' of the distribution shape. For the first three examples $M_4(110) < M_4(101) < M_4(011)$. The kurtosis for any 'impurity' like split band is usually much larger than a wide hybridized band. This is reflected in the above inequality.

4. Conclusion

In this paper we have proposed a methodology to study the electronic structure of random ternary alloys. This is a

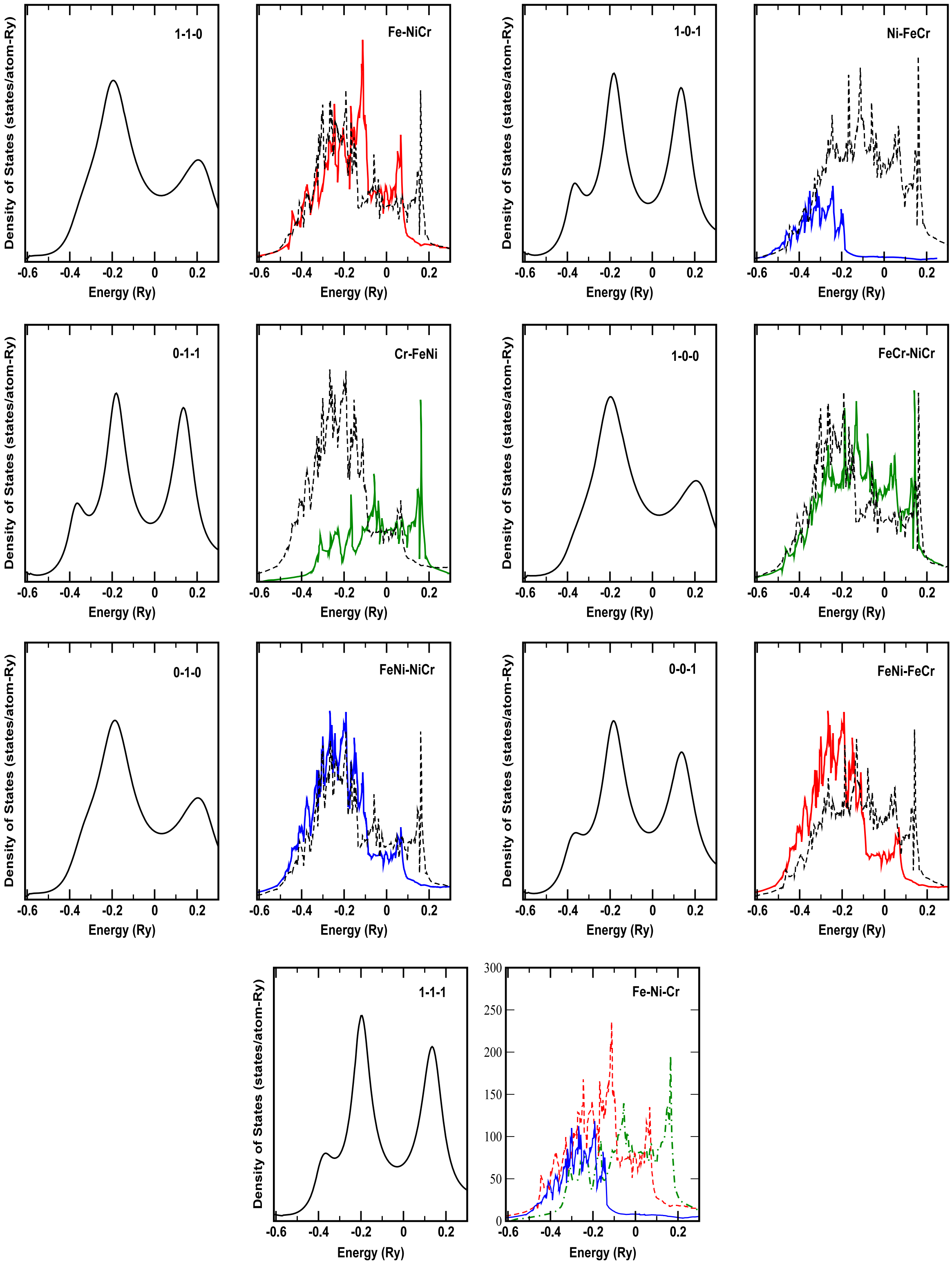

Figure 4. Densities of states for various values of the Warren–Cowley parameters for the ternary alloy. The averaged densities of states are compared with the densities of states of the pure constituents and the corresponding ordered binary alloys. The label (1-1-0) refers to $\alpha_{AB} = 1, \alpha_{AC} = 1$ and $\alpha_{BC} = 0$. Top panel, second and fourth graphs: dashed curves refer to NiCr and full curves to Fe or Ni, respectively. Second panel, second and fourth graphs: dashed curves refer to FeNi and NiCr and full curves to Cr and NiCr, respectively. Third panel, second and fourth graphs: dashed curves refer to NiCr and FeCr and full curves to FeNi in both graphs. Bottom panel, second graph: full curve refers to Ni, dashed to Fe and dashed–dotted to Cr.

generalization of the density functional self-consistent tight-binding linear muffin-tin orbital augmented space recursion (TB-LMTO-ASR) for random binary alloys. We have also indicated, in detail, how to incorporate short range order in the ternary alloys through binary correlations between the constituents. The implementation of the methodology, which

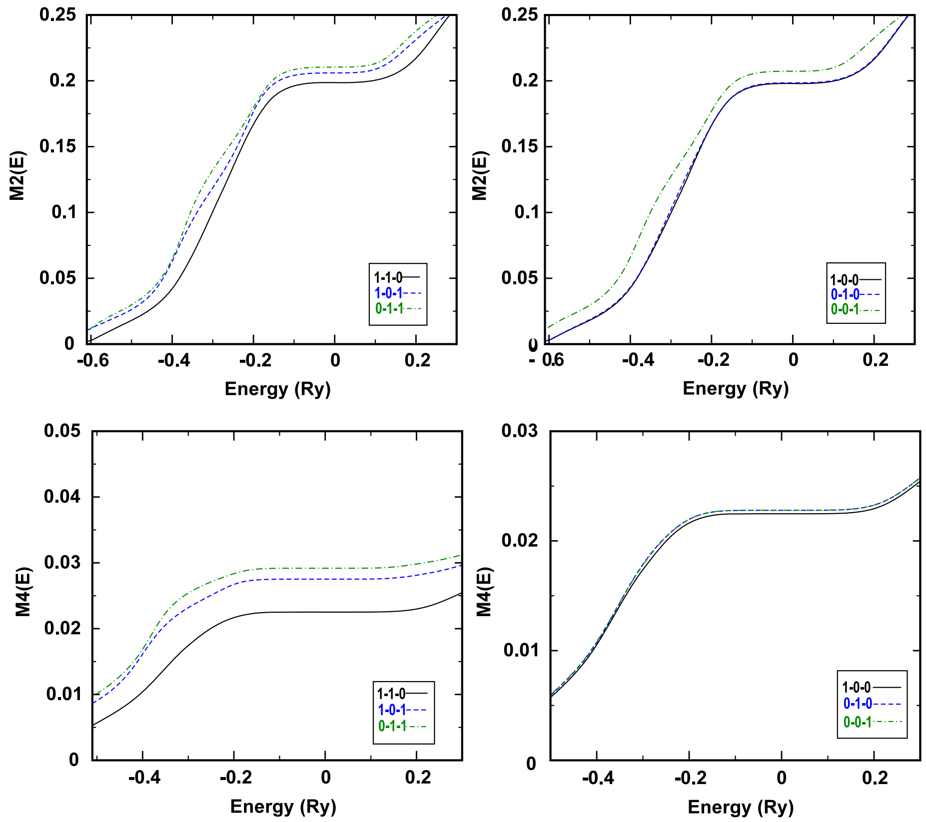

Figure 5. Second and fourth energy moments of the density of states for the examples shown in figure 4.

takes into account the effect of configuration fluctuations beyond those for the coherent potential approximation and based on the ASR maintains the necessary symmetry properties and analyticities of the configuration averaged Green functions, is certainly feasible. We have applied our method to the stainless steel alloy and two other compositions in the Fe–Ni–Cr ternary series. In this paper we have not analyzed magnetism in stainless steel. This analysis, which may involve the study of non-collinear magnetism and spin-glass like phases, we shall keep for a later communication.

Acknowledgments

We would like to thank O K Andersen, Ove Jepsen and co-workers at MPI-Stuttgart for allowing us to use their TB-LMTO program as a basis for our TB-LMTO-ASR routines.

Appendix

An explicit expression for the operator $\tilde{N}_{R_k}$ can be given here:

$$
\begin{aligned}
\tilde{N}_{R_k} &= \left[P^{(1)}_{R_0}\otimes N^{(1)}_{R_k} + P^{(0)}_{R_0}\otimes N^{(0)}_{R_k} + P^{(\bar{1})}_{R_0}\otimes N^{(\bar{1})}_{R_k}\right]\otimes I\otimes\cdots \\
&= \big[V_1\,\tilde{I} + V_2\,\tilde{\mathcal{P}}^1_{R_0} + V_3\tilde{\mathcal{P}}^2_{R_0} + V_4\tilde{\mathcal{P}}^0_{R_k} + V_5\tilde{\mathcal{P}}^2_{R_k} + V_6\tilde{\mathcal{T}}^{01}_{R_0} \\
&\quad + V_7\tilde{\mathcal{T}}^{12}_{R_0} + \cdots + V_8\tilde{\mathcal{T}}^{02}_{R_0} + V_9\tilde{\mathcal{T}}^{01}_{R_k} + V_{10}\tilde{\mathcal{T}}^{12}_{R_k} \\
&\quad + V_{11}\tilde{\mathcal{P}}^0_{R_0}\otimes\tilde{\mathcal{P}}^0_{R_k} + V_{12}\tilde{\mathcal{P}}^0_{R_0}\otimes\tilde{\mathcal{P}}^2_{R_k} + \cdots + V_{13}\tilde{\mathcal{P}}^2_{R_0}\otimes\tilde{\mathcal{P}}^0_{R_k} \\
&\quad + V_{14}\tilde{\mathcal{P}}^2_{R_0}\otimes\tilde{\mathcal{P}}^2_{R_k} + V_{15}\tilde{\mathcal{P}}^0_{R_0}\otimes\tilde{\mathcal{T}}^{01}_{R_k} + V_{16}\tilde{\mathcal{P}}^0_{R_0}\otimes\tilde{\mathcal{T}}^{12}_{R_k} + \cdots \\
&\quad + V_{17}\tilde{\mathcal{P}}^2_{R_0}\otimes\tilde{\mathcal{T}}^{01}_{R_k} + V_{18}\tilde{\mathcal{P}}^2_{R_0}\otimes\tilde{\mathcal{T}}^{12}_{R_k} + V_{19}\tilde{\mathcal{T}}^{01}_{R_0}\otimes\tilde{\mathcal{P}}^0_{R_k} \\
&\quad + V_{20}\tilde{\mathcal{T}}^{01}_{R_0}\otimes\tilde{\mathcal{P}}^2_{R_k} + \cdots + V_{21}\tilde{\mathcal{T}}^{12}_{R_0}\otimes\tilde{\mathcal{P}}^0_{R_k} + V_{22}\tilde{\mathcal{T}}^{12}_{R_0}\otimes\tilde{\mathcal{P}}^2_{R_k} \\
&\quad + V_{23}\tilde{\mathcal{T}}^{02}_{R_0}\otimes\tilde{\mathcal{P}}^0_{R_k} + V_{24}\tilde{\mathcal{T}}^{02}_{R_0}\otimes\tilde{\mathcal{P}}^2_{R_k} + \cdots \\
&\quad + V_{25}\tilde{\mathcal{T}}^{01}_{R_0}\otimes\tilde{\mathcal{T}}^{01}_{R_k} + V_{26}\tilde{\mathcal{T}}^{01}_{R_0}\otimes\tilde{\mathcal{T}}^{12}_{R_k} + V_{27}\tilde{\mathcal{T}}^{12}_{R_0}\otimes\tilde{\mathcal{T}}^{01}_{R_k} \\
&\quad + V_{28}\tilde{\mathcal{T}}^{12}_{R_0}\otimes\tilde{\mathcal{T}}^{12}_{R_k} + \cdots + V_{29}\tilde{\mathcal{T}}^{02}_{R_0}\otimes\tilde{\mathcal{T}}^{01}_{R_k} \\
&\quad + V_{30}\tilde{\mathcal{T}}^{02}_{R_0}\otimes\tilde{\mathcal{T}}^{12}_{R_k}\big].
\end{aligned}
\tag{19}
$$

The different coefficients $V_i;\ i = 1, 30$ are given in terms of $x_A, x_B, x_C, h_1, h_2, h_3, g_1, g_2, g_3, a_1^{(j)}, a_2^{(j)}, a_3^{(j)}, b_1^{(j)}$ and $b_2^{(j)}$ as

$$V_1 = x_B a_1^{(1)} + h_2^2 a_1^{(2)} + g_2^2 a_1^{(3)}$$

$$V_2 = x_1 a_1^{(1)} + h_{x_1} a_1^{(2)} + g_{x_1} a_1^{(3)}$$

$$V_3 = x_2 a_1^{(1)} + h_{y_1} a_1^{(2)} + g_{y_1} a_1^{(3)}$$

$$V_4 = x_B d_1 + h_2^2\,\mathrm{d}x_1 + g_2^2\,\mathrm{d}x_2$$

$$V_5 = x_B d_2 + h_2^2\,\mathrm{d}y_1 + g_2^2\,\mathrm{d}y_2$$

$$V_6 = \sqrt{x_A x_B}\,a_1^{(1)} + h_1 h_2 a_1^{(2)} + g_1 g_2 a_1^{(3)}$$

$$V_7 = \sqrt{x_B x_C}\,a_1^{(1)} + h_2 h_3 a_1^{(2)} + g_2 g_3 a_1^{(3)}$$

$$V_8 = \sqrt{x_C x_A}\,a_1^{(1)} + h_3 h_1 a_1^{(2)} + g_3 g_1 a_1^{(3)}$$

$$V_9 = x_B b_1^{(1)} + h_2^2 b_1^{(2)} + g_2^2 b_1^{(3)}$$

$$V_{10} = x_B b_2^{(1)} + h_2^2 b_2^{(2)} + g_2^2 b_2^{(3)}$$

$$V_{11} = x_1 d_1 + h_{x_1}\,\mathrm{d}x_1 + g_{x_1}\,\mathrm{d}x_2$$

$$V_{12} = x_1 d_2 + h_{x_1}\,\mathrm{d}y_1 + g_{x_1}\,\mathrm{d}y_2$$

$$V_{13} = x_2 d_1 + h_{y_1}\,\mathrm{d}x_1 + g_{y_1}\,\mathrm{d}x_2$$

$$V_{14} = x_2 d_2 + h_{y_1}\,\mathrm{d}y_1 + g_{y_1}\,\mathrm{d}y_2$$

$$V_{15} = x_1 b_1^{(1)} + h_{x_1} b_1^{(2)} + g_{x_1} b_1^{(3)}$$

$$V_{16} = x_1 b_2^{(1)} + h_{x_1} b_2^{(2)} + g_{x_1} b_2^{(3)}$$

$$V_{17} = x_2 b_1^{(1)} + h_{y_1} b_1^{(2)} + g_{y_1} b_1^{(3)}$$

$$V_{18} = x_2 b_2^{(1)} + h_{y_1} b_2^{(2)} + g_{y_1} b_2^{(3)}$$

$$V_{19} = \sqrt{x_A x_B}\, d_1 + h_1 h_2\,\mathrm{d}x_1 + g_1 g_2\,\mathrm{d}x_2$$

$$V_{20} = \sqrt{x_A x_B}\, d_2 + h_1 h_2\,\mathrm{d}y_1 + g_1 g_2\,\mathrm{d}y_2$$

$$V_{21} = \sqrt{x_B x_C}\, d_1 + h_2 h_3\,\mathrm{d}x_1 + g_2 g_3\,\mathrm{d}x_2$$

$$V_{22} = \sqrt{x_B x_C}\, d_2 + h_2 h_3\,\mathrm{d}y_1 + g_2 g_3\,\mathrm{d}y_2$$

$$V_{23} = \sqrt{x_C x_A}\, d_1 + h_3 h_1\,\mathrm{d}x_1 + g_3 g_1\,\mathrm{d}x_2$$

$$V_{24} = \sqrt{x_C x_A}\, d_2 + h_3 h_1\,\mathrm{d}y_1 + g_3 g_1\,\mathrm{d}y_2$$

$$V_{25} = \sqrt{x_A x_B}\, b_1^{(1)} + h_1 h_2 b_1^{(2)} + g_1 g_2 b_1^{(3)}$$

$$V_{26} = \sqrt{x_A x_B}\, b_2^{(1)} + h_1 h_2 b_2^{(2)} + g_1 g_2 b_2^{(3)}$$

$$V_{27} = \sqrt{x_B x_C}\, b_1^{(1)} + h_2 h_3 b_1^{(2)} + g_2 g_3 b_1^{(3)}$$

$$V_{28} = \sqrt{x_B x_C}\, b_2^{(1)} + h_2 h_3 b_2^{(2)} + g_2 g_3 b_2^{(3)}$$

$$V_{29} = \sqrt{x_C x_A}\, b_1^{(1)} + h_3 h_1 b_1^{(2)} + g_3 g_1 b_1^{(3)}$$

$$V_{30} = \sqrt{x_C x_A}\, b_2^{(1)} + h_3 h_1 b_2^{(2)} + g_3 g_1 b_2^{(3)}$$

here,

$$\begin{array}{lll} x_1 = x_A - x_B & x_2 = x_C - x_B & d_1 = a_1^{(1)} - a_2^{(1)} \\ d_2 = a_3^{(1)} - a_2^{(1)} & h_{x_1} = h_1 - h_2 & h_{y_1} = h_3 - h_2 \\ d_{x_1} = a_1^{(2)} - a_2^{(2)} & d_{y_1} = a_3^{(2)} - a_2^{(2)} & g_{x_1} = g_1 - g_2 \\ g_{y_1} = g_3 - g_2 & d_{x_2} = a_1^{(3)} - a_2^{(3)} & d_{y_2} = a_3^{(3)} - a_2^{(3)}. \end{array} \tag{20}$$

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