

A 'first-principles' theory for magnetic correlations and atomic short-range order in paramagnetic alloys. I

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 5981

(<http://iopscience.iop.org/0953-8984/6/30/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 19:02

Please note that [terms and conditions apply](#).

# A ‘first-principles’ theory for magnetic correlations and atomic short-range order in paramagnetic alloys: I

M F Ling†, J B Staunton† and D D Johnson‡

† Department of Physics, University of Warwick, Coventry, UK

‡ Computational Materials Science Department, Sandia National Laboratories, Livermore, CA, USA

Received 25 March 1994, in final form 20 May 1994

**Abstract.** A formalism is derived for describing both magnetic correlations and atomic short-range order (ASRO) in the paramagnetic state of a magnetic alloy. It is based on a ‘first-principles’, finite-temperature, electronic density-functional, mean-field grand potential of the random alloy in which the thermally induced spin fluctuations are modelled in terms of ‘local moments’. For proper comparison, calculations based on this work should be tested against data from experiments on samples at ‘high temperature’ (either *in situ* or rapidly quenched). The calculated ASRO can be compared to any atomic diffuse-scattering data, whereas the calculated magnetic correlations must be compared to polarized-neutron diffuse-scattering data.

## 1. Introduction

Over the past decade or so, the problem of the nature of the paramagnetic state of itinerant magnetic metals has been solved to some extent, at least in principle [2]. A picture of itinerant electrons moving in the fields set up by spin fluctuations whose orientational degrees of freedom slowly vary has proved useful. This arises from the assumption that, on a time scale,  $\tau$ , long compared to an electronic ‘hopping’ time, the spins of the electrons are sufficiently correlated to leave the magnetization (averaged over this time  $\tau$  and over a unit cell in the crystal lattice) non-zero. The orientations of these local magnetizations,  $\{\hat{e}_i\}$ , vary slowly while their magnitudes fluctuate rapidly on the time scale  $\tau$ . The magnitude of the average magnetization on a site  $k$  is defined as the local moment,  $\mu_k = \mu_k(\{\hat{e}_i\})$ , and it changes with the orientational configuration. Whilst this basic scenario is broadly accepted to be capable of providing an adequate description of many metal magnets at elevated temperatures, an assessment of the severity of the neglect of the dynamical effects of the spin fluctuations, an aspect emphasized by several people [3–5], has not been made. Assuming, however, the validity of this static ‘local-moment’ description of the paramagnetic state of itinerant magnets, there remains a long-standing controversy concerning which orientational configurations of the moments are the most important. To date most work on this issue has focused on the pure 3d transition-metal magnets so in this article we bring the discussion around to alloys where the scope for testing the various models of the paramagnetic state is much greater.

The various approaches can be roughly partitioned into two. Firstly, there is the picture of the ‘fluctuating-local-band’ (FLB) theory [6] of a large amount of short-range magnetic order even in the paramagnetic phase. This consists of large spatial regions in which the local moments are nearly aligned, i.e. where the orientations vary gradually. In these regions

conventional Stoner theory can be applied and perturbations to it made. The quasi-elastic, neutron-scattering experiments of Ziebeck *et al* [7], later confirmed by Shirane *et al* [8], are given a simple though not uncontroversial [9] interpretation by this picture. In the case of inelastic neutron scattering, however, even the basic observations are controversial, let alone their interpretation in terms of 'spin waves above  $T_c$ ' that may feature in such a model. In the FLB model, it is difficult to carry out 'first-principles' calculations in which both the magnetic and electronic structures are mutually consistent and consequently to examine the full implications of the model and to improve it systematically.

The second type of approach refers to 'disordered local moments' (DLM) [9–11] and here the local moments are commonly thought to fluctuate fairly independently. This picture was first set up by assuming a Hubbard Hamiltonian, transforming the partition function  $Z$  for the system of interacting electrons into a functional integral over fluctuating fields to which non-interacting electrons are coupled and making static and single-site approximations. Hasegawa has extended this framework to alloys [12]. Gyorffy *et al* [13] set up a 'first-principles' theory based on a generalization of spin-density-functional (SDF) theory which incorporated the effects of orientational spin fluctuations. A scheme for carrying out calculations consistent with a DLM picture was described and results given for iron and nickel [14, 15]. The DLM approach was described as a mean-field theory and it was shown how, in principle, it can be improved systematically.

A scenario in between these two limiting cases has been proposed by Heine and Joynt [16] and Samson [17]. They too were guided by the apparent substantial magnetic SRO above  $T_c$  in Fe and Ni deduced from neutron-scattering data and they emphasize how the orientational magnetic disorder involves a balance in the free energy between energy and entropy. This balance is delicate and requires a consistency to be maintained between the magnetic and electronic structures. Heine and Joynt show that it is possible for the system to disorder on a coarser than atomic length scale. Luchini and Heine [18], however, determined effective 'local-moment' interactions for BCC Fe from the basis of full spd tight-binding calculations for various random orientational configurations. Self-consistency with respect to the sizes of the local moments was not sought. The interactions, including many-atom interactions, were used to fit a Hamiltonian for a Monte Carlo simulation by Chana *et al* [19] who concluded that the large SRO inferred from quasi-elastic neutron-scattering data [7] could not be explained by electronic-structure calculations based on static orientational configurations.

In the light of some of these issues, we describe an extension of the 'first-principles' DLM work to compositionally disordered alloys in this paper and we also detail how the atomic short-range order (ASRO) can be affected by the magnetic fluctuations so that measurements of x-ray and the nuclear component of neutron scattering can be used to test not only the ASRO deduced from the theory but also the description of the paramagnetic state of these alloys itself.

Earlier work [13–15] in which the DLM picture was implemented presented results of explicit calculations for BCC iron of the magnitudes of the local moments,  $\langle \mu_i \{ \hat{e}_k \} \rangle_{\hat{e}_i} = \mu_i(\hat{e}_i) = \bar{\mu} = 1.91\mu_B$  where the partial average  $\langle \mu_i \{ \hat{e}_k \} \rangle_{\hat{e}_i}$  means the average over all configurations with the specific orientation  $\hat{e}_i$  at the site  $i$ .  $T_c$  was estimated to be 1280 K and the uniform paramagnetic susceptibility followed a Curie–Weiss behaviour [20]. A 'local exchange splitting' was predicted for the underlying electronic structure of the paramagnetic phase confirmed to some extent by experiment. While all these theoretical results compared favourably with experimental measurements, for nickel,  $\bar{\mu}$  was found to be zero and the theory reduced to the conventional Stoner model with all its shortcomings including a Curie temperature of  $\sim 3000$  K. As noted by Sandratskii and Kubler [21] and others, the

magnitudes of the 'local moments' in Ni depend strongly upon the the orientations of their surrounding moments and so a mean-field average provided by the DLM approach of this quantity turns out to be zero.

Recently [22] the 'first-principles' theory has been improved substantially by incorporating the idea of Onsager cavity fields to deal with the effects of correlations between the local moments in an approximate way.  $T_c$  for iron is now estimated at 1015 K (experimental value 1040 K) and the spin correlation length as a function of temperature extracted from the wave-vector-dependent susceptibility compares well with the values quoted by Shirane *et al* [8] from an interpretation of the neutron-scattering data. The description of the paramagnetic state of Ni also fits in with similar data and, moreover, the estimated Curie temperature is now 450 K and in fair agreement with the experimental value of 660 K. The uniform susceptibility also follows a Curie-Weiss behaviour in agreement with experiment, a feature which had been lacking hitherto.

In summary, the application of the theory to the paramagnetic state of iron and nickel found that iron can be related superficially to a Heisenberg model whereas nickel can be analysed in terms of traditional Stoner theory, although the magnetic fluctuations have drastically renormalized the exchange interaction and lowered  $T_c$ . This relative success has prompted the extension described in this paper to compositionally disordered alloys. The expectation is that this theoretical treatment should enable a reasonable 'first-pass' description of their paramagnetic states to be made.

In the next section, we describe our theory for the paramagnetic state of compositionally disordered alloys, in which the magnetic fluctuations are modelled in terms of slowly varying orientational 'transverse' components whose sizes vary on the faster time scale and depend upon the orientational environment. A theory for the wave-vector-dependent susceptibility is presented and related to the magnetic correlations inherent in the paramagnetic phase. An analysis of the sorts of effect that might be encountered by this approach in various transition metal alloys is given. The following section sets out the theory for the compositional correlations and therefore atomic short-range order in these alloys. In a companion paper, II [1], we describe the first application of the formalism. Explicit calculations are presented for  $Mn_{15}Cu_{85}$ , which forms a 'spin glass' at low temperatures. The final section draws some conclusions from the work as a whole.

## 2. Magnetic correlations in the paramagnetic state of alloys

In this section we present the details of our theory for describing the growth of magnetic correlations in an alloy as it is cooled from high temperatures. The alloy is assumed to be uniformly compositionally disordered throughout—in other words the rate of cooling is sufficiently fast that little atomic diffusion can take place. We consider a binary alloy,  $A_cB_{1-c}$ , where  $c$  describes the concentration of the A species when averaging over all possible arrangements of A and B atoms. The basic physical insight underlying much recent work on metallic magnetism and described in the introduction assumes that it is possible to identify fast and slow motions in the interacting electron system. Let us consider a particular distribution of nuclei on the lattice  $\{\xi_i\}$ , where  $\xi_i = 1$  (or 0) if site  $i$  in the lattice is occupied by an A (or B) atom. On a time scale,  $\tau$ , long in comparison with the electronic hopping time ( $\hbar/W \simeq 10^{-15}$  s, where  $W$  represents a relevant band width) but short when compared with an appropriate 'spin fluctuation' time ( $\hbar/\omega_{SF} \simeq 10^{-15}$  s, where  $\omega_{SF}$  characterizes a typical spin fluctuation frequency), the correlation between spin orientations of electrons leaving a site set up a finite magnetization,  $M_\tau(r_i, \{\xi_i\})$ , if this quantity is averaged over the time  $\tau$ . The orientations of these 'local moments' vary slowly on this time scale.

The many-electron system, while ergodic, is assumed not to cover its phase space uniformly in time and can be imagined as being restricted for long times  $\tau$  near points in its phase space which can be labelled by particular orientational arrangements of the local moments and then moving rapidly to another point in phase space. Each orientational arrangement of this alloy with a compositional structure labelled by  $\{\xi_i\}$  can be annotated by the set of unit vectors  $\{\hat{e}_i\}$  picking out the orientations of the local moments,

$$\hat{e}_i = \int_{V_i} d\mathbf{r}_i M_\tau(\mathbf{r}_i, \{\xi_i\}) \Big/ \left| \int_{V_i} d\mathbf{r}_i M_\tau(\mathbf{r}_i, \{\xi_i\}) \right| \quad (1)$$

where  $V_i$  is the volume of the  $i$ th unit cell, and  $\mathbf{r}_i = \mathbf{r}_l - \mathbf{R}_i$  and  $\mathbf{R}_i$  is a lattice vector. A generalization of the spin-density-functional theory [13] provides a short time ( $\ll \tau$ ) description of the system labelled by  $\{\hat{e}_i\}$  in terms of a 'generalized' grand potential  $\Omega(\{\xi_i\}, \{\hat{e}_i\})$  which is followed by a prescription for the corresponding time evolution of the system in the reduced phase space of such configurations.

By generalizing the finite-temperature SDF theory [13, 23] one can write down formally that  $\Omega(\{\xi_i\}, \{\hat{e}_i\})$  is obtained as a result of a functional minimization of the grand-potential functional

$$\begin{aligned} \Omega[\rho(\mathbf{r}); M(\mathbf{r})] = & \int d\mathbf{r} V^{\text{ext}}(\mathbf{r}, \{\xi_i\})\rho(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & + T_s[\rho, M] - T S_s[\rho, M] + \Omega_{\text{xc}}[\rho, M] \end{aligned} \quad (2)$$

with  $T_s$  and  $S_s$  being respectively the kinetic energy and entropy of a system of non-interacting electrons with densities  $\rho(\mathbf{r})$  and  $M(\mathbf{r})$  at a temperature  $T$ .  $V^{\text{ext}}(\{\xi_i\})$  describes the particular arrangement of nuclei under study. As is well known, this functional minimization can be achieved from the solution of appropriate single-electron Kohn-Sham equations. The functional minimization in this problem, where the slowly varying spin fluctuations have been separated out, is carried out subject to the constraint that the magnetization on every site is orientated consistently with  $\{\hat{e}_i\}$ , i.e.  $\int_{V_i} d\mathbf{r}_i M(\mathbf{r}_i, \{\hat{e}_i\}) \times \hat{e}_i = 0$ . By incorporating Lagrange multipliers, the minimization closely follows conventional SDF theory.

The long-time averages appropriate to the second stage of the scheme can be evaluated by taking averages over the ensemble of orientational configurations  $\{\hat{e}_i\}$  with measure

$$P(\{\xi_i\}, \{\hat{e}_i\}) = \exp[-\beta\Omega(\{\xi_i\}, \{\hat{e}_i\})] \Big/ \prod_j \int d\hat{e}_j \exp[-\beta\Omega(\{\xi_j\}, \{\hat{e}_j\})]. \quad (3)$$

The free energy is found from  $F\{\xi_i\} = -(1/\beta) \ln \prod_j \int d\hat{e}_j \exp(-\beta\Omega(\{\xi_j\}, \{\hat{e}_j\}))$ . The role of a classical 'spin' (local-moment) Hamiltonian, albeit a highly complicated one, is played by  $\Omega(\{\xi_j\}, \{\hat{e}_j\})$ . By choosing a suitable reference 'spin' Hamiltonian,  $\Omega_0 = \sum_i \omega_i(\hat{e}_i)$  and expanding about it using the Feynman-Peierl-Bogoliubov inequality [24], an approximation to the free energy is obtained and a mean-field theory constructed. The Feynman-Peierl-Bogoliubov inequality is given by  $F \leq F_0 + \langle \Omega - \Omega_0 \rangle^0 = \bar{F}$  with  $F_0 = -(1/\beta) \ln \prod_i \int d\hat{e}_i \exp(-\beta\Omega_0)$ , and, for any quantity  $X$ ,

$$\langle X \rangle^0 = \prod_i \int d\hat{e}_i P_0(\{\hat{e}_i\}) X(\{\hat{e}_i\}). \quad (4)$$

Here,  $\omega_i(\hat{e}_i)$  is given by  $\langle \Omega(\{\xi_i\}, \{\hat{e}_i\}) \rangle_{\hat{e}_i = \hat{e}_i'}$  in which the orientations of the local moments on all the sites (apart from site  $i$ ) are averaged over. On site  $i$ , the moment is constrained to

point along  $\hat{e}'_i$ . Details have been discussed elsewhere [13] for the case of pure metals. In principle, this analysis should be repeated for every configuration of nuclei  $\{\xi_j\}$  and suitable averages made, consistent with the requirement that, for the high-temperature disordered state, sites are occupied by A nuclei with probability  $c$  and the remainder by B with probability  $(1 - c)$ .

Here, in order to construct a tractable scheme, the coherent potential approximation (CPA) [25], is used to average the electronic motion over both the 'local-moment' orientations and the compositional configurations. This provides a single-site averaging scheme for (4). We assume that each site is randomly occupied by A or B nuclei such that a fraction  $c$  of the sites are occupied by A nuclei. But in the event that a particular site  $i$  is occupied by an A nucleus, it has a chance

$$P_{i,A}(\hat{e}_i) = \exp(-\beta \langle \Omega(\{\hat{e}_j\} \{ \xi_j \}) \rangle_{\hat{e}_i, A_i}) / \sum_{\alpha=A,B} \int d\hat{e}'_i \exp(-\beta \langle \Omega(\{\hat{e}_j\}, \{ \xi_j \}) \rangle_{\hat{e}'_i, \alpha_i}) \quad (5)$$

of its local moment pointing along  $\hat{e}_i$  ( $P_0(\{\hat{e}_i\}) = \prod_i [P_{i,A}(\hat{e}_i) + P_{i,B}(\hat{e}_i)]$ ).  $c = \int d\hat{e}_i P_{i,A}(\hat{e}_i)$  and  $(1 - c) = \int d\hat{e}_i P_{i,B}(\hat{e}_i)$ . An inhomogeneous version of the CPA is required in that the effective CPA medium can be different from site to site reflecting the inhomogeneous probability distribution  $P_{i,A(B)}(\hat{e}_i)$  [26, 27]. Now the solution to the Kohn-Sham equations can be written down in terms of an effective single-electron Green function accessible from the self-consistent-field, Korringa-Kohn-Rostoker, electronic-multiple-scattering theory in combination with the coherent potential approximation (SCF-KKR-CPA) [28, 29]. This approach was designed originally for non-magnetic, binary alloys but here we use a generalization so that the orientational arrangements of the local moments are also averaged over. It follows that we have charge and magnetization densities apportioned to each site

$$\rho_{i,\alpha}(\mathbf{r}_i, \hat{e}_i) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \nu_e) \text{Tr}(\mathbf{G}(\mathbf{r}_i, \mathbf{r}_i; \epsilon))_{\hat{e}_i, \alpha_i} \quad (6)$$

$$M_{i,\alpha}(\mathbf{r}_i, \hat{e}_i) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \nu_e) \hat{e}_i \text{Tr}(\boldsymbol{\sigma} \cdot \hat{e}_i \mathbf{G}(\mathbf{r}_i, \mathbf{r}_i; \epsilon))_{\hat{e}_i, \alpha_i} = \mu_{i,\alpha}(\hat{e}_i) \hat{e}_i \quad (7)$$

where  $\alpha$  denotes whether an A or B atom is located on that site.  $\nu_e$  is the electronic chemical potential,  $\mathbf{G}$  represents a Kohn-Sham Green function expressed as a  $2 \times 2$  matrix, and  $\boldsymbol{\sigma}$  is the usual set of Pauli's spin matrices.

At temperatures well in excess of any magnetic ordering temperature  $T_c$ , there is an equal chance of a moment being orientated in any given direction on a site  $i$  (therefore,  $P_{i,A}(\hat{e}_i) = c/4\pi$ ,  $P_{i,B}(\hat{e}_i) = (1 - c)/4\pi$  and  $\mu_{i,A(B)}(\hat{e}_i) = \bar{\mu}_{A(B)}$ ) and so there is zero magnetization overall, i.e.

$$M_i = \int \hat{e}_i (P_{i,A}(\hat{e}_i) \mu_{i,A}(\hat{e}_i) + (1 - c) \mu_{i,B}(\hat{e}_i)) d\hat{e}_i = \frac{1}{4\pi} \int \hat{e}_i (c \bar{\mu}_A + (1 - c) \bar{\mu}_B) d\hat{e}_i = 0. \quad (8)$$

Nonetheless, local moments  $\bar{\mu}_A$  and  $\bar{\mu}_B$  and therefore 'local exchange splitting' can exist in this paramagnetic state [13]. The SCF-KKR-CPA methodology delivers a description of this paramagnetic, disordered-local-moment (DLM) state of alloys. The local exchange splitting can introduce important features in the electronic structure of these alloys which would not be present in a conventional Stoner-type description of their paramagnetic state [15, 30]. Experimental probes of the electronic structure can therefore be used to test the validity of this DLM model of the important spin fluctuations in the paramagnetic state.

The formal representation of the charge and magnetization densities (equations (6) and (7)) within multiple-scattering formalism of the SCF-KKR-CPA method is described briefly in appendix A, which uses the notation of Faulkner and Stocks [31]. We refer the reader to this appendix for particular details. This approach connects the properties of the underlying electronic structure to those of the macroscopic system and allows us to require only the atomic numbers of the constituents of the alloy as input into our subsequent calculations.

Accepting that we can calculate the Green function of equations (6) and (7), we now move on to our main focus of magnetic correlations. This is based on a theory for the paramagnetic, static, spin susceptibility of the system,  $\chi(q, T)$ , in which the response of the system to a small, inhomogeneous magnetic field is considered. The technical details are a generalization to those used to derive an expression for the paramagnetic susceptibility of a pure metal which have been described fully elsewhere [15, 22]. A small magnetic field  $\{h_i\}$  is applied to the paramagnetic system. This induces small deviations  $\{\delta P_{i,A}(\hat{e}_i)\}$ ,  $\{\delta P_{i,B}(\hat{e}_i)\}$  from the equilibrium single-site distribution functions  $P_{i,A}^0(\hat{e}_i) = c/4\pi$  and  $P_{i,B}^0(\hat{e}_i) = (1-c)/4\pi$  and to the sizes of the local moments  $\{\delta\mu_{i,A}\}$ ,  $\{\delta\mu_{i,B}\}$ . As a consequence, the local magnetization,  $M_i$ , after averaging over nuclear configurations may be written as

$$\begin{aligned} M_i &= \frac{c}{4\pi} \int \hat{e}_i \delta\mu_{i,A}(\hat{e}_i) d\hat{e}_i + \frac{(1-c)}{4\pi} \int \hat{e}_i \delta\mu_{i,A}(\hat{e}_i) d\hat{e}_i + c\bar{\mu}_A \int \hat{e}_i \delta P_i^A(\hat{e}_i) d\hat{e}_i \\ &\quad + (1-c)\bar{\mu}_B \int \hat{e}_i \delta P_i^B(\hat{e}_i) d\hat{e}_i \\ &= c\mu_{i,A} + (1-c)\mu_{i,B} + \bar{\mu}_{i,A}m_{i,A} + \bar{\mu}_{i,B}m_{i,B} \end{aligned} \quad (9)$$

and correspondingly the susceptibility,  $\chi_{ij} = \partial M_i / \partial h_j^{\text{ext}}$ , takes the form

$$\chi_{ij} = c\chi_{ij,A}^{\mu} + (1-c)\chi_{ij,B}^{\mu} + c\chi_{ij,A}^m + (1-c)\chi_{ij,B}^m = \chi_{ij}^{\mu} + \chi_{ij}^m. \quad (10)$$

Evidently the first two terms in equation (10) describe how the magnitude of the local moments responds to external field, whereas the third and fourth terms describes how they tend to align with the field.

The derivation follows that of Staunton and Gyorffy [22] who incorporated the ideas of Onsager cavity fields [33] into a first-principles theory for the paramagnetic phases of magnetic metals such that those changes (i.e.,  $\{\delta\mu_{j,A}^{(i)}\}$ ,  $\{\delta\mu_{j,B}^{(i)}\}$ ,  $\{\bar{\mu}_A\delta m_{j,A}^{(i)}\}$ , and  $\{\bar{\mu}_B\delta m_{j,B}^{(i)}\}$ ) that are derived from  $M_i$  (the induced magnetization at site  $i$ ) and, which contribute to the setting up of this magnetization, are subtracted out. In other words, corrections are introduced that are still compatible with the single-site model and averaging. As a consequence, the CPA medium (characterized by the single-site scattering matrices,  $\{t_{c,j}\}$ , given in appendix A) is altered by the applied magnetic field and the induced inhomogeneous magnetization (i.e.  $t_{c,j}^{-1} \simeq t_{c,j}^{-1} \mathbb{1} + \delta t_{c,j}^{-1} \sigma_z$ ), in such a way that these CPA adjustments,  $\{\delta t_{c,j}^{-1}\}$ , contributing to  $M_i$  at a site  $i$  also do not contain a component which is directly produced by  $M_i$ . In this fashion, the treatment of the electronic structure and the description of the spin fluctuations are compatible with each other.

From equations (5) and (7), expressions for the components  $\mu_{i,\alpha}(\hat{e}_i)$  and  $m_{i,\alpha}$  can be written down (with  $\alpha$  either the A or B species) in the following form:

$$\begin{aligned} \mu_{i,\alpha} &= \sum_{j \neq i} [\gamma_{ij,\alpha A}^{\mu m} (m_{j,A} - \delta m_{j,A}^{(i)}) + \gamma_{ij,\alpha B}^{\mu m} (m_{j,B} - \delta m_{j,B}^{(i)}) \\ &\quad + \gamma_{ij,\alpha A}^{\mu\mu} (\mu_{j,A} - \delta\mu_{j,A}^{(i)}) + \gamma_{ij,\alpha B}^{\mu\mu} (\mu_{j,B} - \delta\mu_{j,B}^{(i)})] + \sum_j \chi_{ij,\alpha}^0 h_j^{\text{ext}} \end{aligned} \quad (11)$$

$$\begin{aligned}
m_{i,\alpha} = & \frac{\beta}{3} \sum_{j \neq i} [(J_{ij,\alpha A}^{mm} (m_{j,A} - \delta m_{j,A}^{(i)}) + J_{ij,\alpha B}^{mm} (m_{j,B} - \delta m_{j,B}^{(i)})) \\
& + (J_{ij,\alpha A}^{m\mu} (\mu_{j,A} - \delta \mu_{j,A}^{(i)}) + J_{ij,\alpha B}^{m\mu} (\mu_{j,B} - \delta \mu_{j,B}^{(i)}))] + \frac{\beta}{3} \bar{\mu}_\alpha h_i^{\text{ext}}. \quad (12)
\end{aligned}$$

In the above equations, the lattice Fourier transform of the quantities  $J_{ij,\alpha\beta}^{mm}$ ,  $J_{ij,\alpha\beta}^{m\mu}$ ,  $\gamma_{ij,\alpha\beta}^{\mu\mu}$ ,  $\gamma_{ij,\alpha\beta}^{\mu\mu}$ , and  $\chi_{ij,\alpha}^0$  are specified completely in terms of the multiple-scattering formalism in appendix B and are accessible from our SCF-KKR-CPA calculations performed for the compositionally disordered, paramagnetic state.

To complete the derivation, following Staunton and Gyorffy [22], we suppose that the Onsager corrections are given by  $\delta \mu_{j,\alpha}^{(i)} = \chi_{ji,\alpha}^\mu \chi_{ii}^{-1} M_i$  and  $\delta m_{j,\alpha}^{(i)} = \chi_{ji,\alpha}^m \chi_{ii}^{-1} M_i$ . As a result, and after a lattice Fourier transform, we obtain the following key set of equations:

$$\begin{aligned}
\chi_\alpha^\mu(q) = & [\gamma_{\alpha A}^{\mu\mu}(q) - c\Lambda_\alpha^\mu] \chi_A^\mu(q) + [\gamma_{\alpha B}^{\mu\mu}(q) - (1-c)\Lambda_\alpha^\mu] \chi_B^\mu(q) \\
& + [\gamma_{\alpha A}^{\mu m}(q) - \bar{\mu}_A \Lambda_\alpha^\mu] \chi_A^m(q) / \bar{\mu}_A + [\gamma_{\alpha B}^{\mu m}(q) - \bar{\mu}_B \Lambda_\alpha^\mu] \chi_B^m(q) / \bar{\mu}_B + \chi_\alpha^0(q) \quad (13)
\end{aligned}$$

$$\begin{aligned}
\chi_\alpha^m(q) = & \frac{1}{3} \beta c_\alpha \bar{\mu}_\alpha \{ \bar{\mu}_\alpha + [J_{\alpha A}^{m\mu}(q) - c\Lambda_\alpha^m] \chi_A^\mu(q) + [J_{\alpha B}^{m\mu}(q) - (1-c)\Lambda_\alpha^m] \chi_B^\mu(q) \\
& + [J_{\alpha A}^{mm}(q) - \bar{\mu}_A \Lambda_\alpha^m] \chi_A^m(q) / \bar{\mu}_A + [J_{\alpha B}^{mm}(q) - \bar{\mu}_B \Lambda_\alpha^m] \chi_B^m(q) / \bar{\mu}_B + \Sigma_\alpha(q) \}. \quad (14)
\end{aligned}$$

The total wave-vector-dependent susceptibility,  $\chi(q)$ , is given from (10) by the sum of the four terms  $\chi_A^\mu(q)$ ,  $\chi_B^\mu(q)$ ,  $\chi_A^m(q)$ , and  $\chi_B^m(q)$ . The Onsager cavity corrections  $\Lambda_\alpha^\mu$  and  $\Lambda_\alpha^m$  are given by

$$\Lambda_\alpha^\mu = \chi_{ii}^{-1} \int dq [\gamma_{\alpha A}^{\mu\mu}(q) \chi_A^\mu(q) + \gamma_{\alpha B}^{\mu\mu}(q) \chi_B^\mu(q) + \gamma_{\alpha A}^{\mu m}(q) \chi_A^m(q) / \bar{\mu}_A + \gamma_{\alpha B}^{\mu m}(q) \chi_B^m(q) / \bar{\mu}_B] \quad (15)$$

$$\Lambda_\alpha^m = \chi_{ii}^{-1} \int dq [J_{\alpha A}^{m\mu}(q) \chi_A^\mu(q) + J_{\alpha B}^{m\mu}(q) \chi_B^\mu(q) + J_{\alpha A}^{mm}(q) \chi_A^m(q) / \bar{\mu}_A + J_{\alpha B}^{mm}(q) \chi_B^m(q) / \bar{\mu}_B] \quad (16)$$

and thus complete the description of the high-temperature susceptibility in terms of the electronic properties.

In the paramagnetic phase of a ferromagnetic alloy,  $\chi(q)$  is largest at small wave-vectors, i.e.  $|q| \simeq 0$ , which is compatible with ferromagnetic correlations. On the other hand, an alloy with  $\chi(q)$  peaking at finite values of  $|q|$  has anti-ferromagnetic-type correlations which may lead to an anti-ferromagnetically ordered state at lower temperatures. The magnetic transition temperature  $T_c$  is that temperature at which  $\chi(q)$  diverges.

To illustrate the physical meaning of the above equations we consider some interesting limiting cases. In the limit of  $c = 1$ , i.e. a pure metal, we obtain the results of Staunton and Gyorffy [22], where

$$\chi^m(q) = \frac{\frac{1}{3} \beta \bar{\mu} [\bar{\mu} + (J^{m\mu}(q) - \Lambda^m) \chi^\mu(q) + \Sigma(q)]}{(1 - \frac{1}{3} \beta (J^{mm}(q) - \bar{\mu} \Lambda^m))} \quad (17)$$

$$\chi^\mu(q) = \frac{[\gamma^{\mu m}(q) - \bar{\mu} \Lambda^\mu] \chi^m(q) / \bar{\mu} + \chi^0(q)}{(1 - [\gamma^{\mu\mu}(q) - \Lambda^\mu])}. \quad (18)$$



For a rigid-local moment system, Fe being a fairly good example of such a system,  $\chi(q) \simeq \chi^m(q)$  and  $J^{\mu\mu}(q)$ ,  $\gamma^{\mu\mu}(q)$ ,  $\gamma^{\mu\mu}(q)$  and  $\chi^0(q)$  are all small. Equation (17) then has the form of a classical Heisenberg model within the spherical approximation, with 'spins' of magnitude  $\bar{\mu}$ . On the other hand, in a system such as Ni, where no 'local moment' is set up on the average in the paramagnetic phase,  $\bar{\mu} = 0$  and  $J^{mm}(q)$ ,  $J^{m\mu}(q)$ , and  $\gamma^{\mu\mu}(q)$  also vanish and  $\chi^m(q) = 0$ . As such,  $\chi(q) = \chi^\mu(q) = \chi^0(q)/[1 - \gamma^{\mu\mu}(q) + \Lambda^\mu]$  with  $\Lambda^\mu = (\chi_{ii}^0)^{-1} \int dq \gamma^{\mu\mu}(q) \chi^\mu(q)$ . Note that  $\chi(q)$  is a product of Stoner exchange-correlation term and a Pauli susceptibility  $\chi^0(q)$ . The susceptibility evidently describes an enhanced Stoner paramagnet where the exchange-correlation effects have been renormalized by the spin fluctuations. The paramagnetic phases of weak itinerant ferromagnets have been described in this form by other approaches [3-5].

For an alloy, i.e.  $c \neq 0$ , in which neither alloying species has a local moment ( $\text{Ni}_c\text{Pt}_{1-c}$  may be such an example of an alloy system), our expression for the total susceptibility becomes essentially a generalization of that for a Stoner paramagnet to alloys. Here, the quantities  $J_{\alpha,\beta}^{mm}$ ,  $J_{\alpha,\beta}^{m,\mu}$ ,  $\Sigma_\alpha$ , and  $\gamma_{\alpha,\beta}^{\mu m}$  all vanish and  $\chi(q) \simeq \chi_A^\mu(q) + \chi_B^\mu(q)$ . A third case refers to those alloys in which  $\bar{\mu}_A \neq 0$  and  $\bar{\mu}_B = 0$  with the B species showing little response to magnetic field. The magnetic response is almost entirely provided by the A moments altering their orientations so that the susceptibility has the form of that of a classical Heisenberg model in which a fraction  $c$  of the sites are occupied by A 'spins'. The quantity  $J_{AA}^{mm}(q)$  represents the lattice Fourier transform of  $J_{ij,AA}^{mm}$  which describes the 'exchange' interaction between two A atoms occupying site  $i$  and  $j$  averaged over the compositional configurations in the  $A_cB_{1-c}$  alloy. Examples are  $\text{Mn}_c\text{Cu}_{1-c}$  alloys. In the low-Mn-concentration region ( $c \leq 0.25$ ) the local moments are set up almost entirely on the Mn sites while the Cu host (as we shall see in the companion paper II [1]) plays an important intermediary role. The Mn moments vary in both magnitude and orientation and interact with each other via the Cu host. The nature of these interactions is at least to some extent responsible for the 'spin-glass' behaviour of  $\text{Mn}_c\text{Cu}_{1-c}$  alloys at low temperatures.

Another class of alloy is constituted of two atomic species which both respond strongly to the magnetic field although local moments establish themselves only on lattice sites associated with one of the species, the A species say. Nickel-rich FCC  $\text{Fe}_c\text{Ni}_{1-c}$  and iron-rich BCC  $\text{Fe}_c\text{V}_{1-c}$  alloys may be examples of this type. Here, with B referring to Ni,  $J_{BB}^{mm}$ ,  $J_{AB}^{mm}$ ,  $J_{BA}^{mm}$ ,  $J_{BA}^{m\mu}$ ,  $J_{BB}^{m\mu}$ ,  $\Sigma_B$ ,  $\gamma_{AB}^{\mu m}$  and  $\gamma_{BB}^{\mu m}$  are all zero. Finally, in alloys with non-zero moments on both A and B sites, e.g.  $\text{Fe}_c\text{Co}_{1-c}$  alloys, we have a mixture of all effects.

### 3. Compositional correlations in alloys and their dependence on the nature of the paramagnetic state

Over the past few years, progress has been made in describing trends in phase diagrams of alloys from detailed models of their electronic structure [34-39]. In the compositionally disordered state at high temperatures, the compositional correlations often act as precursors to the type of ordered alloy that forms as the alloy is cooled. The framework of concentration waves [26, 27, 40] is ideal for the purpose of describing these correlations. In two recent papers [41, 42], the details of a theory were provided for the compositional correlations based on the electronic structure of the high-temperature random state using the SCF-KKR-CPA. The calculated chemical susceptibility,  $\alpha(q)$ , (which is the lattice Fourier transform of the compositional correlation function  $\alpha_{ij}$ , or Warren-Cowley short-range order parameters), can be compared with diffuse x-ray and neutron-scattering data. A tendency for the alloy to phase segregate at low temperatures is indicated by  $\alpha(q)$  peaking at  $q = (0, 0, 0)$ , whereas

alloys which tend to order are characterized by  $\alpha(q)$  having maximum values at a finite  $q$ . The particular wave-vector specifies the appropriate concentration wave which describes the corresponding ordered structure which is likely to form at lower temperatures.

A strength of this work is that the statistical mechanics of the compositional fluctuations are dealt with within a 'mean-field' approximation which is consistent with the mean-field description of the electronic structure calculated within the inhomogeneous CPA [27, 43]. Both aspects are improved by incorporating Onsager cavity fields once again. This ensures that the diffuse intensity is conserved over the Brillouin zone, atypical of most mean-field theories; hence, with this description, the diagonal part of the fluctuation-dissipation theorem is obeyed. Although the theory described in [41, 42] includes both 'band-filling' and 'charge-rearrangement' effects, such as 'charge transfer', resulting from the so-called double-counting contributions to the energetics, the effects of spin fluctuations were neglected. In this section, therefore, we present a generalization to this approach and demonstrate how the compositional ordering tendencies in the paramagnetic alloy can be affected by the presence of spin fluctuations. If the spin fluctuations are to be modelled in terms of 'local moments', as discussed in the last section, a local exchange splitting is introduced into the paramagnetic electronic structure which may have a profound effect upon the nature of the compositional correlations exhibited by the alloy above any compositional transition temperature. This provokes a novel suggestion for an experimental test of the models of the paramagnetic state in multi-component metallic systems. We propose that diffuse x-ray and neutron-scattering measurements of the atomic short-range order (ASRO) in alloys be used to test the DLM picture of the paramagnetic state alongside similar scrutinies of other models of the paramagnetic state.

As far as possible, we shall follow the notation of Staunton *et al* and Johnson *et al* [41, 42] which provide the details of our theory for the compositional correlation function of non-magnetic alloys. Our starting point is the separation of electronic and chemical degrees of freedom. The electronic motion (including the spin fluctuations generated by the many interacting electrons which are particularly relevant here) happens on a time scale  $> 10^{-12}$  s, which is vastly different from the times typically taken for atoms to diffuse (seconds to years). It is therefore useful to describe any alloy configuration (whether ordered or disordered) in terms of Ising-like, site-occupation variables,  $\{\xi_i\}$ , previously defined. The thermodynamic average of  $\xi_i$ , i.e.  $\langle \xi_i \rangle$ , is then the probability of an A atom being found at that site, or the average concentration  $c_i$ . For a homogeneously disordered alloy at high temperatures,  $c_i = c$  for all sites. We want to predict the type of site-occupational correlations which develop to break this symmetry as the alloy is cooled.

In the context of spin-density-functional theory, the grand potential  $\tilde{\Omega}(\{\xi_i\})$  for a paramagnetic system of interacting electrons moving in the fields set up by an arrangement  $\{\xi_i\}$  of nuclei occupying the sites on a crystal lattice behaves as a Hamiltonian for the site-occupational variables. If the paramagnetic system is to be modelled by 'local moments' in which there is an equal chance of a moment pointing in any direction, the  $\tilde{\Omega}(\{\xi_i\}) = \prod_j (1/4\pi) \int d\hat{e}_j \Omega(\{\xi_i\}, \{\hat{e}_j\})$  where an average is taken over the moments' orientations. The probability of a particular configuration  $\{\xi_i\}$  is then given by  $P(\{\xi_i\}) = \exp(-\beta\tilde{\Omega}(\{\xi_i\}))/Z$  where the partition function  $Z = \sum_{\xi_k} \exp(-\beta\tilde{\Omega}(\{\xi_i\}) - \nu \sum_i \xi_i)$ . The alloy chemical potential difference,  $\nu$ , preserves the relative numbers of A and B atoms (not to be confused with the electronic chemical potential used in defining the electronic charge and magnetization densities, as in equations (6) and (7)). We shall assume that the compositionally disordered phase is always paramagnetic so that the compositional transition temperature is higher than any magnetic ordering temperature. This is not always

the case and there are situations where magnetic structure can have a profound effect upon compositional ordering tendencies [44].

At very high temperatures, the alloy is (assumed to be) homogeneously disordered. This provides the reference state for a linear response investigation of the atomic pair correlations which grow as the temperature is lowered. The KKR-CPA electronic-structure techniques to which we have referred already are then employed to describe this high-temperature reference state. If a small, inhomogeneous, 'external' chemical potential,  $\{\delta v_i\}$ , is applied to the homogeneous random state, local variations of the site-occupational probabilities are induced and can be calculated from linear-response theory. As a result, the compositional correlation function, and the growth of correlations with lowering temperatures, can be investigated via the fluctuation-dissipation theorem which connects these responses to the atomic pair-correlation function,  $\alpha_{ij} = \delta c_i / \delta v_j = \beta(\langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle)$ .

We make use of the Feynman-Peierls-Bogoliubov inequality [24] to estimate the free energy of the system  $F = -(1/\beta) \ln Z$  which results in the 'Hamiltonian'  $\tilde{\Omega}(\{\xi_i\})$  being replaced by a mean-field Hamiltonian,  $\Omega_{\text{MF}}(\{\xi_i\}) = \sum_i (\delta \langle \tilde{\Omega} \rangle / \delta c_i) \xi_i = \sum_i S_i^{(1)} \xi_i$ . The functional  $S_i^{(1)}$  can formally be expressed in terms of quantities available from the inhomogeneous SCF-KKR-CPA. It is now straightforward, within this mean-field approach, to find the probability that an A atom is located at a site  $i$ ,

$$c_i = \frac{\exp(-\beta(S_i^{(1)} + v_i))}{[\exp(-\beta(S_i^{(1)} + v_i)) + 1]} \quad (19)$$

which tends to a uniform  $c$  at very high temperatures for a uniform chemical potential difference  $v_i = v$ . By allowing  $\{v_i\}$  to have a weak site dependence, i.e.  $\{v_i = v + \delta v_i\}$ , we can write down an expression for the induced change to the probability of finding an A atom on the site  $k$ ,  $\delta c_k$ , to lowest order in the applied potential. It depends on the changes induced on all the other sites, i.e.

$$\delta c_k = \beta c(1-c) \left[ \sum_j \frac{\delta S_k^{(1)}}{\delta c_j} \delta c_j + \delta v_k \right] = \beta c(1-c) \left[ \sum_j S_{kj}^{(2)} \delta c_j + \delta v_k \right]. \quad (20)$$

The term in square brackets specifies an analogue of the Weiss field of mean-field theories of magnetism. The mean-field treatment can be improved in a similar manner by replacing these 'Weiss' fields by Onsager cavity fields [41, 42]. Accordingly, the cavity field on a particular site  $i$  must be chosen such that the variation  $\delta c_i$  on that site no longer includes the effects from the induced change of concentration on that site. We find

$$\delta c_i = \beta c(1-c) \left[ \sum_j S_{ij}^{(2)} (\delta c_j - \delta c_j^{(\delta c_i)}) + \delta v_i \right] = \beta c(1-c) \delta v_i^{\text{cavity}} \quad (21)$$

where  $\delta c_j^{(\delta c_i)}$  is the change in concentration on a site  $j$  due to the change  $\delta c_i$  on the site  $i$ . Following [41, 42], we choose  $\delta c_j^{(\delta c_i)}$  to be  $\alpha_{ji} \delta v_i^{\text{cavity}}$ . Since  $\delta v_i^{\text{cavity}}$  is  $\delta c_i / (\beta c(1-c))$  from the equation above,  $\delta c_j^{(\delta c_i)} = \alpha_{ji} \delta c_i / (\beta c(1-c))$ . The site-diagonal part of the fluctuation-dissipation theorem,  $\alpha_{ii} = \beta c(1-c)$ , is automatically guaranteed by this prescription.

In terms of concentration wave-vectors, following a lattice Fourier transform, we can write

$$\alpha(q) = \frac{\beta c(1-c)}{[1 - \beta c(1-c)(S^{(2)}(q) - \Lambda^c)]} \quad (22)$$

with

$$\Lambda^c = \frac{1}{\beta c(1-c)} \int d\mathbf{q} S^{(2)}(\mathbf{q}) \alpha(\mathbf{q}). \quad (23)$$

These are the equations analogous to the Gorsky–Bragg–Williams model [45] although altered by the cavity fields.  $S^{(2)}(\mathbf{q})$  plays the role of the lattice Fourier transform of an atomic interchange energy. In the two previous papers [41, 42], in common with much previous work, we have discussed how it is dependent on various attributes of the interacting electron system including the average number of valence electrons, d-electron band width, and charge transfer. Most preceding work on this topic has neglected magnetic effects. Here we highlight the role of spin fluctuations in the paramagnetic state of alloys.

In the presence of an applied, inhomogeneous chemical potential  $\{\delta v_i\}$ , the concentration changes  $\{\delta c_i\}$  are accompanied by a rearrangement of charge associated with each site,  $\{\delta \rho_{i,A(B)}\}$ , and, in a DLM paramagnetic system, also by adjustments to the magnitudes of the local moments  $\{\delta \mu_{i,A(B)}\}$ . These alterations are all interdependent as shown in the following expressions:

$$\begin{aligned} \delta c_i = \beta c(1-c) \delta v_i^{\text{cavity}} = \beta c(1-c) \delta v_i^{\text{cavity}} (\{\delta c_j - \delta c_j^{(\delta c_i)}\}, \{\delta \rho_{j,A} - \delta \rho_{j,A}^{(\delta c_i)}\}, \\ \{\delta \rho_{j,B} - \delta \rho_{j,B}^{(\delta c_i)}\}, \{\delta \mu_{j,A} - \delta \mu_{j,A}^{(\delta c_i)}\}, \{\delta \mu_{j,B} - \delta \mu_{j,B}^{(\delta c_i)}\}) \end{aligned} \quad (24)$$

$$\begin{aligned} \delta \rho_{i,A(B)}(\mathbf{r}_i) = \delta \rho_{i,A(B)}(\mathbf{r}_i; \{\delta c_j - \delta c_j^{(\delta c_i)}\}, \{\delta \rho_{j,A} - \delta \rho_{j,A}^{(\delta c_i)}\}, \{\delta \rho_{j,B} - \delta \rho_{j,B}^{(\delta c_i)}\}, \\ \{\delta \mu_{j,A} - \delta \mu_{j,A}^{(\delta c_i)}\}, \{\delta \mu_{j,B} - \delta \mu_{j,B}^{(\delta c_i)}\}) \end{aligned} \quad (25)$$

$$\begin{aligned} \delta \mu_{i,A(B)}(\mathbf{r}_i) = \delta \mu_{i,A(B)}(\mathbf{r}_i; \{\delta c_j - \delta c_j^{(\delta c_i)}\}, \{\delta \rho_{j,A} - \delta \rho_{j,A}^{(\delta c_i)}\}, \{\delta \rho_{j,B} - \delta \rho_{j,B}^{(\delta c_i)}\}, \\ \{\delta \mu_{j,A} - \delta \mu_{j,A}^{(\delta c_i)}\}, \{\delta \mu_{j,B} - \delta \mu_{j,B}^{(\delta c_i)}\}). \end{aligned} \quad (26)$$

These expressions show that the charge and local magnetization rearrangements must also include the effects of the cavity-field corrections. In terms of response functions (namely,  $\alpha_{ik} = dc_i/dv_k$ ,  $\rho_{i,k,A(B)} = d\rho_{i,A(B)}(\mathbf{r}_i)/dv_k$ ,  $\mu_{i,k,A(B)} = d\mu_{i,A(B)}(\mathbf{r}_i)/dv_k$ ), the Onsager corrections can be written as  $\delta c_j^{(\delta c_i)} = \alpha_{ji} \delta c_i / (\beta c(1-c))$ ,  $\delta \rho_{j,A}^{(\delta c_i)} = \rho_{ji,A(B)} \delta c_i / (\beta c(1-c))$ , and  $\delta \mu_{j,A}^{(\delta c_i)} = \mu_{ji,A(B)} \delta c_i / (\beta c(1-c))$ , see [41].

Before an explicit expression for the atomic pair-correlation function,  $\alpha(\mathbf{q})$ , can be written down in terms of the underlying electronic structure of the homogeneously disordered, paramagnetic alloy, it is necessary to determine the induced changes to the charge densities,  $\delta \rho_{i,A(B)}(\mathbf{r}_i)$ , and to the local moment sizes,  $\delta \mu_{i,A(B)}(\mathbf{r}_i)$ , which develop on each site and vary throughout each unit cell. The spatial forms of these changes must be obtained from the self-consistent-field formalism and not by imposing a particular functional form for the spatial variation,  $\mathbf{r}_i$ , in each unit cell. A computationally cost-effective method is set up by expanding the  $\{\delta \rho_{i,A(B)}\}$  in terms of a small set of basis functions,  $f_n(\mathbf{r}_i)$ , so that  $\delta \rho_{i,A(B)}(\mathbf{r}_i) = \delta \rho_{i,A(B)}^n f_n(\mathbf{r}_i)$  and  $\delta \rho_{i,A(B)}^n = \int d\mathbf{r}_i \delta \rho_{i,A(B)}(\mathbf{r}_i) f_n(\mathbf{r}_i)$ . The functions satisfy  $\int d\mathbf{r}_i f_n(\mathbf{r}_i) f_{n'}(\mathbf{r}_i) = \delta_{nn'}$  and  $\int d\mathbf{r}_i \delta \rho_{i,A(B)}(\mathbf{r}_i) = \delta \rho_{i,A(B)}^1 \delta_{n1} u_1$  where  $u_1$  is equal to the square root of the unit cell volume. We found three to four functions of the type discussed in [41] to be adequate which reflects the fact that charge-density variations occur predominantly in the outer regions of the unit cells.

The problem of calculating the variation of the local magnetization within each unit cell, on the other hand, must be treated quite differently. The formation of the local moments is a cooperative phenomenon predominantly involving d-electrons and consequently the

variation of the  $\{\delta\mu_{i,A(B)}\}$  within each unit cell is rather different from the charge variations. We assume that the moment changes take on a spatial dependence which is extracted (in the form of four magnetic scaling functions  $f_{\alpha\uparrow(\downarrow)}^m(\mathbf{r}_i)$ ) from only the spin- and spatially resolved densities of states at the Fermi energy i.e.  $n_{\alpha\uparrow(\downarrow)}(\mathbf{r}_i, \varepsilon_F) = -\text{Im}\langle G_{\uparrow(\downarrow)}(\mathbf{r}_i, \mathbf{r}_i; \varepsilon_F) \rangle_{\alpha}$ . This latter choice of scaling property reflects that the changes to the sizes of the moments are predominantly due to the changes to the electronic structure around the Fermi energy [46].

As shown schematically in the above expressions, the response functions  $\alpha_{ij}$ ,  $\rho_{ij,A(B)}^n$ , and  $\mu_{ij,A(B)}$  are all connected. This coupling is manifest in the changes to the CPA medium which occur as the inhomogeneous chemical potential is applied. These alterations can also be dealt within our linear-response theory and account for the cavity-field corrections. By considering the lattice Fourier transforms of  $\alpha_{ij}$ ,  $\rho_{ij,A(B)}^n$ , and  $\mu_{ij,A(B)}$ , namely  $\alpha(\mathbf{q})$ ,  $\rho_{A(B)}^n(\mathbf{q})$ , and  $\mu_{A(B)}(\mathbf{q})$ , we obtain the following key equations:

$$\alpha(\mathbf{q}) = \beta c(1-c) + \beta c(1-c)[(S^{cc}(\mathbf{q}) - \Lambda^c)\alpha(\mathbf{q}) + \sum_n (S_A^{cp;n}(\mathbf{q})\rho_A^n(\mathbf{q}) + S_B^{cp;n}(\mathbf{q})\rho_B^n(\mathbf{q})) + S_A^{c\mu}(\mathbf{q})\mu_A(\mathbf{q}) + S_B^{c\mu}(\mathbf{q})\mu_B(\mathbf{q}) - (S^{cP}(\mathbf{q}) + \Delta Q)P(\mathbf{q})C(\mathbf{q})] \quad (27)$$

$$\rho_{A(B)}^n(\mathbf{q}) = (\epsilon_{A(B)}^{\rho c;n'}(\mathbf{q}) - \Lambda_{A(B)}^{\rho c;n'})\alpha(\mathbf{q}) + \sum_n (\epsilon_{A,A(B)}^{\rho\rho;n'n}(\mathbf{q})\rho_A^n(\mathbf{q}) + \epsilon_{B,A(B)}^{\rho\rho;n'n}(\mathbf{q})\rho_B^n(\mathbf{q})) + \epsilon_{A,A(B)}^{\rho\mu}(\mathbf{q})\mu_A(\mathbf{q}) + \epsilon_{B,A(B)}^{\rho\mu}(\mathbf{q})\mu_B(\mathbf{q}) - \epsilon_{A(B)}^{\rho P;n'}(\mathbf{q})P(\mathbf{q})C(\mathbf{q}) \quad (28)$$

$$\mu_{A(B)}(\mathbf{q}) = (\epsilon_{A(B)}^{\mu c}(\mathbf{q}) - \Lambda_{A(B)}^{\mu c})\alpha(\mathbf{q}) + u_1\epsilon_{A,A(B)}^{\mu\rho}(\mathbf{q})\rho_A^1(\mathbf{q}) + u_1\epsilon_{B,A(B)}^{\mu\rho}(\mathbf{q})\rho_B^1(\mathbf{q}) + u_1\epsilon_{A,A(B)}^{\mu\mu}(\mathbf{q})\mu_A(\mathbf{q}) + u_1\epsilon_{B,A(B)}^{\mu\mu}(\mathbf{q})\mu_B(\mathbf{q}) - u_1\epsilon_{A(B)}^{\mu P}(\mathbf{q})P(\mathbf{q})C(\mathbf{q}). \quad (29)$$

$P(\mathbf{q}) = (c\rho_A^1(\mathbf{q}) + (1-c)\rho_B^1(\mathbf{q}))u_1 + \Delta Q\alpha(\mathbf{q})$  is the  $\mathbf{q}$ -dependent variation from charge neutrality, or effective polarization caused by the short-range order. ( $\Delta Q$  is the 'charge transfer' in the homogeneously disordered alloy, i.e. the difference in charges when a site is occupied by an A atom and when it is then occupied by a B atom.)  $C(\mathbf{q})$  is the lattice Fourier transform of the Coulomb interaction  $1/|\mathbf{R}_i - \mathbf{R}_j|$ . The Onsager cavity corrections  $\Lambda^c$ ,  $\Lambda_{A(B)}^{\rho c;n'}$ , and  $\Lambda_{A(B)}^{\mu c}$  are given by

$$\Lambda^c = \frac{1}{\beta c(1-c)} \int d\mathbf{q} \left[ S^{cc}(\mathbf{q})\alpha(\mathbf{q}) + \sum_n (S_A^{cp;n}(\mathbf{q})\rho_A^n(\mathbf{q}) + S_B^{cp;n}(\mathbf{q})\rho_B^n(\mathbf{q})) + S_A^{c\mu}(\mathbf{q})\mu_A(\mathbf{q}) + S_B^{c\mu}(\mathbf{q})\mu_B(\mathbf{q}) - (S^{cP}(\mathbf{q}) + \Delta Q)P(\mathbf{q})C(\mathbf{q}) \right] \quad (30)$$

$$\Lambda_{A(B)}^{\rho c;n'} = \frac{1}{\beta c(1-c)} \int d\mathbf{q} \left[ \epsilon_{A(B)}^{\rho c;n'}(\mathbf{q})\alpha(\mathbf{q}) + \sum_n (\epsilon_{A,A(B)}^{\rho\rho;n'n}(\mathbf{q})\rho_A^n(\mathbf{q}) + \epsilon_{B,A(B)}^{\rho\rho;n'n}(\mathbf{q})\rho_B^n(\mathbf{q})) + u_1\epsilon_{A,A(B)}^{\rho\mu}(\mathbf{q})\mu_A(\mathbf{q}) + u_1\epsilon_{B,A(B)}^{\rho\mu}(\mathbf{q})\mu_B(\mathbf{q}) - \epsilon_{A(B)}^{\rho P;n'}(\mathbf{q})P(\mathbf{q})C(\mathbf{q}) \right] \quad (31)$$

$$\Lambda_{A(B)}^{\mu c} = \frac{1}{\beta c(1-c)} \int d\mathbf{q} \left[ \epsilon_{A(B)}^{\mu c}(\mathbf{q})\alpha(\mathbf{q}) + \sum_n (\epsilon_{A,A(B)}^{\mu\rho;n}(\mathbf{q})\rho_A^n(\mathbf{q}) + \epsilon_{B,A(B)}^{\mu\rho;n}(\mathbf{q})\rho_B^n(\mathbf{q})) + u_1\epsilon_{A,A(B)}^{\mu\mu}(\mathbf{q})\mu_A(\mathbf{q}) + u_1\epsilon_{B,A(B)}^{\mu\mu}(\mathbf{q})\mu_B(\mathbf{q}) - \epsilon_{A(B)}^{\mu P}(\mathbf{q})P(\mathbf{q})C(\mathbf{q}) \right]. \quad (32)$$

Expressions for all the quantities are detailed in the appendix. They are all calculable from the electronic structure of the compositionally disordered, DLM-paramagnetic state and hence depend on any 'local exchange splitting' that may be present.

The compositional correlation function  $\alpha(\mathbf{q})$  is obtained from the solution to the six equations shown above and has the Ornstein-Zernicke form

$$\alpha(\mathbf{q}) = \frac{\beta c(1-c)}{[1 - \beta c(1-c)(S^{(2)}(\mathbf{q}) - \Lambda^c)]} \quad (33)$$

where the 'interchange' energy  $S^{(2)}(\mathbf{q})$  can be expressed as a sum of three components

$$S^{(2)}(\mathbf{q}) = S^{cc}(\mathbf{q}) + S^{\text{cross}}(\mathbf{q}) - (\Delta Q)^2 C(\mathbf{q}) / (1 + l_{\text{scr}}^2 C(\mathbf{q})). \quad (34)$$

The first term derives from the filling of the electronic states and has been discussed at length by several authors when spin fluctuation effects are neglected [27, 35, 47]. It relates to the Hume-Rothery electron-per-atom-ratio rule. The other two terms describe the contributions to the interchange energy which occur as the charge and local moment magnitudes rearrange as a consequence of the atomic short-range order. The second of these two terms describes an electrostatic ('charge-transfer'-like) piece and depends on the Coulomb interaction  $C(\mathbf{q})$  and an inverse screening length  $l^{\text{scr}}$  which is determined by the electronic structure. Such effects for alloys in which magnetic effects are unimportant have been discussed in the two earlier articles [41, 42]. In brief,  $S^{(2)}(\mathbf{q})$  depends on the nature of the electronic structure of the compositionally disordered, paramagnetic state.

#### 4. Conclusion

We have presented a theory for the magnetic and compositional correlations in paramagnetic alloys based on our 'first-principles' disordered-local-moments (DLM) description of the high-temperature, paramagnetic state of a magnetic transition-metal alloy. This work is a natural extension of the DLM theory developed by Gyorffy and Staunton *et al* [13, 20] for magnetic metals and by Staunton *et al* and Johnson *et al* [41, 42] for non-magnetic alloys. A strength of the present work is that while the statistical mechanics of compositional and magnetic fluctuations have been treated in a mean-field framework, the idea of Onsager cavity fields has been incorporated so that the diagonal part of the fluctuation-dissipation theorem is obeyed. The expression for the static, paramagnetic susceptibility  $\chi(\mathbf{q})$  was derived by considering the response of the system to the application of a small external magnetic field, and it contains two essential parts. One describes the tendency of the local moments to align with the magnetic field, and the other measures the change in the size of the moments. The expression for the compositional correlation function  $\alpha(\mathbf{q})$ , on the other hand, was obtained by considering the effect of applying an external 'chemical-potential change' to the system, and it has the standard Ornstein-Zernicke form. We have emphasized how a 'local exchange splitting' of the electronic structure, by allowing for the presence of local moments in the paramagnetic state of the compositionally disordered alloy, can have a profound effect upon the alloy's tendency to order or phase segregate.

#### Acknowledgments

This work was supported in part by the SERC in the UK and by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Science through a new-initiative grant under contract No DE-AC04-94AL85000 with Sandia.

## Appendix A

Here, we mention a few formal results which will be useful in the derivations for the quantities described in terms of electronic structure. Multiple-scattering formalism in the notation of Faulkner and Stocks [31] is used to describe the Kohn–Sham Green function

$$\langle \mathbf{G}(\mathbf{r}_i, \mathbf{r}'_i; \epsilon) \rangle_{\hat{e}_i, \alpha i} = \sum_{LL'} (Z_{L, \alpha}(\mathbf{r}_i) \langle \tau_{LL'}^{ii} \rangle_{\hat{e}_i, \alpha i} Z_{L', \alpha}^\dagger(\mathbf{r}_i) - Z_{L, \alpha}(\mathbf{r}_i^<) J_{L', \alpha}(\mathbf{r}_i^>)) \quad (\text{A1})$$

where  $Z_{L, \alpha}(\mathbf{r}_i)$  is the regular solution of the single-site Schrödinger equation appropriate to the  $i$ th lattice site, occupied by an  $\alpha$  (A or B atom), and  $J_{L, \alpha}(\mathbf{r}_i)$  is the irregular solution.  $\langle \cdot \rangle_{\hat{e}_i, \alpha i}$  denotes an average over all local moment orientations and compositional arrangements with the restriction that the site  $i$  is occupied by an A (B) nucleus and its local moment is directed along  $\hat{e}_i$ .  $\tau^{ij}$  represents the scattering path operator [32] and when it operates on the wave incident at the site at  $\mathbf{R}_j$  it gives the scattered wave coming from the site at  $\mathbf{R}_i$ , including all the effects of scattering in between, i.e.

$$\tau_{LL'}^{ij} = \mathbf{t}_i^{ij} \delta_{ij} \delta_{LL'} + \sum_{k \neq i} \sum_{L''} \mathbf{t}_L^{ik} G^0(\mathbf{R}_i - \mathbf{R}_j; \epsilon) \mathbb{1} \tau_{L''L'}^{kj} \quad (\text{A2})$$

where  $\mathbf{t}_i^l$  describes the angular momentum  $L$ th ( $l, m$ ) channel single-site scattering from site  $i$  and  $G_{LL'}^0$  the structure constants appropriate to the crystal lattice. In the notations for the Green function and scattering matrices above and in the following we use sans-serif bold to indicate  $2 \times 2$  spin matrix structure. Sometimes the angular momentum indices,  $L = l, m$ , are suppressed for brevity.

The idea behind the CPA is to retrieve the Bloch theorem and construct a lattice of effective complex CPA potentials, with single-site scattering  $\mathbf{t}$  matrices  $\mathbf{t}_{c,i}$ , such that the motion of an electron through this lattice approximates the motion of an electron, on the average, through a lattice that is randomly occupied by A and B nuclei and where the local moment associated with a site  $i$  has the chance  $P_{i, \alpha}(\hat{e}_i)$  of pointing in a direction  $\hat{e}_i$  if the site is occupied by an A (B) atom. The multiple scattering in the lattice of CPA scatterers is specified by  $\tau^{C, ij}$ . The CPA *ansatz* [25] is defined by (suppressing the angular-momentum labels)

$$\tau^{C, ii} = \int d\hat{e}_i P_{i, A}(\hat{e}_i) \langle \tau^{ii} \rangle_{\hat{e}_i, A} + \int d\hat{e}_i P_{i, B}(\hat{e}_i) \langle \tau^{ii} \rangle_{\hat{e}_i, B} \quad (\text{A3})$$

which in the homogeneously disordered paramagnetic state ( $P_{i, A}(\hat{e}_i) = c/4\pi$ ) becomes  $\tau^{C, ii} = \tau^{C, ii} \mathbb{1} = \tau^{C, 00} \mathbb{1}$  where

$$\tau^{C, 00} = \frac{1}{2} c (\langle \tau^{00} \rangle_{\uparrow A} + \langle \tau^{00} \rangle_{\downarrow A}) + \frac{1}{2} (1 - c) (\langle \tau^{00} \rangle_{\uparrow B} + \langle \tau^{00} \rangle_{\downarrow B}) \quad (\text{A4})$$

in which the  $\uparrow$  ( $\downarrow$ ) subscript denotes the scattering parallel (anti-parallel) to the local spin polarization  $\hat{e}_i$  and  $\mathbf{t}_{c, i} = t_c \mathbb{1}$ .  $\tau^{C, 00}$  is given by the Brillouin-zone integration of the inverse of the KKR matrix,

$$\tau^{C, 00} = \frac{1}{\Omega_{\text{BZ}}} \int d\mathbf{k} [t_c^{-1} - G(\mathbf{k})]^{-1} \quad (\text{A5})$$

$$\langle \tau^{ii} \rangle_{\hat{e}_i, A(B)} = [\mathbb{1} + (\mathbf{t}_{A(B)}^{-1}(\hat{e}_i) - t_c^{-1} \mathbb{1}) \tau^{C, 00} \mathbb{1}]^{-1} \tau^{C, 00} = D_{A(B)}(\hat{e}_i) \tau^{C, 00} \mathbb{1} \quad (\text{A6})$$

where  $\mathbf{t}_{A(B)}(\hat{e}_i)$  describes the scattering from a site  $i$  occupied by an A (B) atom whose local moment is orientated along  $\hat{e}_i$ . In a 'global' frame of reference, the multiple scattering from a site occupied by an A (B) nucleus with local moment  $\hat{e}_i$  in the homogeneously disordered paramagnetic state can be written as

$$\langle \tau^{ii} \rangle_{\hat{e}_i, A(B)} = \frac{1}{2} (D_{\uparrow, A(B)} + D_{\downarrow, A(B)}) \tau^{C, 00} \mathbb{1} + \frac{1}{2} \sigma \cdot \hat{e}_i (D_{\uparrow, \alpha} - D_{\downarrow, A(B)}) \tau^{C, 00}. \quad (\text{A7})$$

Appendix B

An important step in completing our response-theory formalism with regard to either the response of the paramagnetic, compositionally disordered alloy to an external inhomogeneous magnetic field  $\{h_j^{\text{ext}}\}$  or chemical potential  $\{\nu\}$  is to evaluate  $\delta t_{c,j}^{-1}$ , the corresponding adjustments to the CPA medium. The CPA condition requires that replacing the CPA potential at site  $i$  with an A or B atom, on average, produces no further scattering in the CPA environment. Mathematically, this condition can be expressed by the following matrix equations:

$$\sum_{\alpha=A,B} \int d\hat{e}_i P_{i,\alpha}(\hat{e}_i) X_i^\alpha(\hat{e}_i) = 0 \tag{B1}$$

where  $X_i^\alpha(\hat{e}_i) = [(t_{\alpha,i}^{-1}(\hat{e}_i) - t_{c,ii}^{-1})^{-1} + \tau^{c,ii}]^{-1}$  and  $\tau^{c,ii}$  is found from the calculable quantity  $\{t_{c,q}\}$ . The CPA *ansatz* is appropriate for an inhomogeneous occupational and orientational probability distribution  $\{P_{i,\alpha}\}$ . Our response theory requires that these matrix equations are solved by expanding about the homogeneous SCF-KKR-CPA medium, i.e. in terms of  $\{P_{i,\alpha}(\hat{e}_i) = c/4\pi + \delta P_{i,\alpha}(\hat{e}_i)\}$ . After much tedious algebraic manipulation, we find that the lattice Fourier transform of the response of the CPA medium at a site  $i$  to an applied magnetic field at site  $j$ ,  $h_j^{\text{ext}}$ ,  $\lambda_{\text{mag}}(\mathbf{q}) = \sum_j (\delta t_{c,i}^{-1} / \delta h_j^{\text{ext}}) \exp(i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j))$  involves several components,  $\lambda_{\text{mag}}^{A,m}(\mathbf{q})$ ,  $\lambda_{\text{mag}}^{B,m}(\mathbf{q})$ ,  $\lambda_{\text{mag}}^{A,\mu}(\mathbf{q})$ ,  $\lambda_{\text{mag}}^{B,\mu}(\mathbf{q})$ , and  $\lambda^H(\mathbf{q})$  which we shall specify shortly. Similarly the response of the medium to an inhomogeneous ‘chemical potential’,  $\lambda_{\text{conc}}(\mathbf{q})$ , can also be expressed in terms of components  $\lambda_{\text{conc}}^c(\mathbf{q})$ ,  $\lambda_{\text{conc}}^{A,\rho,n}(\mathbf{q})$ ,  $\lambda_{\text{conc}}^{B,\rho,n}(\mathbf{q})$ ,  $\lambda_{\text{conc}}^{A,\mu,i}(\mathbf{q})$ ,  $\lambda_{\text{conc}}^{B,\mu,i}(\mathbf{q})$ , and  $\lambda^P(\mathbf{q})$  which are set out below.

The most important quantity to evaluate in these quantities and which appears in expressions for the quantities in sections 2 and 3 are the convolutions

$$R_{L_1 \times L_2, L_3 \times L_4}(\mathbf{q}) = \Omega_{\text{BZ}}^{-1} \int d\mathbf{k} \tau_{L_1 L_3}^{c,0}(\mathbf{k}) \tau_{L_4 L_2}^{c,0}(\mathbf{k} + \mathbf{q}) \tag{B2}$$

$$T_{L_1 \times L_2, L_3 \times L_4}(\mathbf{q}) = R_{L_1 \times L_2, L_3 \times L_4}(\mathbf{q}) - \tau_{0, L_1 L_3}^{c,00} \tau_{0, L_4 L_2}^{c,00} \tag{B3}$$

which is the lattice Fourier transform of  $\tau_0^{c,ij} \tau^{c,ji}$ . Here  $L_1$  etc refer to both  $l$  and  $m$  angular-momentum quantum numbers and  $\Omega_{\text{BZ}}$  is the volume of the Brillouin zone. A more detailed discussion on the computational aspect of this quantity is given in [41]. The components of the response of the CPA medium can now be written

$$\lambda_{\text{mag}, L_1 \times L_2}^{\alpha, m(\mu)} = \sum_{L_3 \times L_4} \frac{1}{2} [I_{L_1 \times L_2, L_3 \times L_4}^1(\mathbf{q}) + I_{L_1 \times L_2, L_3 \times L_4}^2(\mathbf{q})]^{-1} \zeta_{\text{mag}, L_3 \times L_4}^{\alpha, m(\mu)} \tag{B4}$$

$$\lambda_{L_1 \times L_2}^{P(H)} = \sum_{L_3 \times L_4} \frac{1}{2} [I_{L_1 \times L_2, L_3 \times L_4}^1(\mathbf{q}) + I_{L_1 \times L_2, L_3 \times L_4}^2(\mathbf{q})]^{-1} \zeta_{L_3 \times L_4}^{P(H)} \tag{B5}$$

$$\lambda_{\text{conc}, L_1 \times L_2}^{c(\alpha), \rho, n} = \sum_{L_3 \times L_4} \frac{1}{2} [I_{L_1 \times L_2, L_3 \times L_4}^1(\mathbf{q}) + I_{L_2 \times L_2, L_3 \times L_4}^2(\mathbf{q})]^{-1} \zeta_{\text{conc}, L_3 \times L_4}^{c(\alpha), \rho, n} \tag{B6}$$

$$\lambda_{\text{conc}, L_1 \times L_2}^{c(\alpha), \mu} = \sum_{L_3 \times L_4} \frac{1}{2} [I_{L_1 \times L_2, L_3 \times L_4}^1(\mathbf{q}) + I_{L_2 \times L_2, L_3 \times L_4}^2(\mathbf{q})]^{-1} \zeta_{\text{conc}, L_3 \times L_4}^{c(\alpha), \mu} \tag{B7}$$



where  $\alpha = A, B$ . The sum of the two normalization integrals,  $I_{L_1 \times L_2}^1(q)$  and  $I_{L_1 \times L_2}^2(q)$ , which describe the full response of the CPA medium, have the form of a Bethe-Salpeter equation. They are given by

$$\begin{aligned} I_{L_1 \times L_2; L_3 \times L_4}^1(q) = & \frac{2}{3} [c(D_{L_1 L_3}^{A, \uparrow} D_{L_4 L_2}^{A, \uparrow} + \frac{1}{2} D_{L_1 L_3}^{A, \uparrow} D_{L_4 L_2}^{A, \downarrow} + \frac{1}{2} D_{L_1 L_3}^{A, \downarrow} D_{L_4 L_2}^{A, \uparrow} + D_{L_1 L_3}^{A, \downarrow} D_{L_4 L_2}^{A, \downarrow}) \\ & + (1-c)(D_{L_1 L_3}^{B, \uparrow} D_{L_4 L_2}^{B, \uparrow} + \frac{1}{2} D_{L_1 L_3}^{B, \uparrow} D_{L_4 L_2}^{B, \downarrow} + \frac{1}{2} D_{L_1 L_3}^{B, \downarrow} D_{L_4 L_2}^{B, \uparrow} + D_{L_1 L_3}^{B, \downarrow} D_{L_4 L_2}^{B, \downarrow})] \\ & - \frac{2}{3} [c(X_{L_1 L_3}^{A, \uparrow} X_{L_4 L_2}^{A, \uparrow} + \frac{1}{2} X_{L_1 L_3}^{A, \uparrow} X_{L_4 L_2}^{A, \downarrow} + \frac{1}{2} X_{L_1 L_3}^{A, \downarrow} X_{L_4 L_2}^{A, \uparrow} + X_{L_1 L_3}^{A, \downarrow} X_{L_4 L_2}^{A, \downarrow}) \\ & + (1-c)(X_{L_1 L_3}^{B, \uparrow} X_{L_4 L_2}^{B, \uparrow} + \frac{1}{2} X_{L_1 L_3}^{B, \uparrow} X_{L_4 L_2}^{B, \downarrow} + \frac{1}{2} X_{L_1 L_3}^{B, \downarrow} X_{L_4 L_2}^{B, \uparrow} + X_{L_1 L_3}^{B, \downarrow} X_{L_4 L_2}^{B, \downarrow})] \\ & \times T_{L \times L_1 L_3, L \times L_4 L_2}(q) \end{aligned} \quad (B8)$$

$$\begin{aligned} I_{L_1 \times L_2; L_3 \times L_4}^2(q) = & \frac{1}{3} [c(D_{L_1 L_3}^{A, \uparrow} D_{L_4 L_2}^{A, \uparrow} - \frac{1}{2} D_{L_1 L_3}^{A, \uparrow} D_{L_4 L_2}^{A, \downarrow} - \frac{1}{2} D_{L_1 L_3}^{A, \downarrow} D_{L_4 L_2}^{A, \uparrow} + D_{L_1 L_3}^{A, \downarrow} D_{L_4 L_2}^{A, \downarrow}) \\ & + (1-c)(D_{L_1 L_3}^{B, \uparrow} D_{L_4 L_2}^{B, \uparrow} - \frac{1}{2} D_{L_1 L_3}^{B, \uparrow} D_{L_4 L_2}^{B, \downarrow} - \frac{1}{2} D_{L_1 L_3}^{B, \downarrow} D_{L_4 L_2}^{B, \uparrow} + D_{L_1 L_3}^{B, \downarrow} D_{L_4 L_2}^{B, \downarrow})] \\ & - \frac{1}{3} [c(X_{L_1 L_3}^{A, \uparrow} X_{L_4 L_2}^{A, \uparrow} - \frac{1}{2} X_{L_1 L_3}^{A, \uparrow} X_{L_4 L_2}^{A, \downarrow} - \frac{1}{2} X_{L_1 L_3}^{A, \downarrow} X_{L_4 L_2}^{A, \uparrow} + X_{L_1 L_3}^{A, \downarrow} X_{L_4 L_2}^{A, \downarrow}) \\ & + (1-c)(X_{L_1 L_3}^{B, \uparrow} X_{L_4 L_2}^{B, \uparrow} - \frac{1}{2} X_{L_1 L_3}^{B, \uparrow} X_{L_4 L_2}^{B, \downarrow} - \frac{1}{2} X_{L_1 L_3}^{B, \downarrow} X_{L_4 L_2}^{B, \uparrow} + X_{L_1 L_3}^{B, \downarrow} X_{L_4 L_2}^{B, \downarrow})] \\ & \times T_{L \times L_1 L_3, L \times L_4 L_2}(q) \end{aligned} \quad (B9)$$

where  $X^{\alpha, \uparrow(\downarrow)} = [(t_{\alpha, i \uparrow(\downarrow)}^{-1} - t_{c, ii}^{-1})^{-1} + \tau^{c, ii}]^{-1}$  with the angular-momentum indices, and  $D^{\alpha, \uparrow(\downarrow)}$  is defined in equation (13).

We now provide detailed expressions for quantities specified in sections 2 and 3. These are quantities involving single-site scattering terms and three integrals over the unit cell (although these are replaced by the Wigner-Seitz sphere in the calculations),

$$F_{\uparrow(\downarrow)L L'}^{\alpha, n} = - \int d\mathbf{r}_i Z_{\uparrow(\downarrow)L}^{\alpha}(\mathbf{r}_i) Z_{\uparrow(\downarrow)L'}^{\alpha}(\mathbf{r}_i) f_n(\mathbf{r}_i) / u_i \quad (B10)$$

$$U_{\uparrow(\downarrow)L L'}^{\alpha \mu} = - \int d\mathbf{r}_i Z_{\uparrow(\downarrow)L}^{\alpha}(\mathbf{r}_i) \left[ \frac{d v_{xc}(\mathbf{r}_i)}{d \mu_{\alpha}} + (-) \frac{d v_{xc}(\mathbf{r}_i)}{d \mu_{\alpha}} \right] f_{\alpha \uparrow(\downarrow)}^m(\mathbf{r}_i) Z_{\uparrow(\downarrow)L'}^{\alpha}(\mathbf{r}_i) \quad (B11)$$

$$\begin{aligned} U_{\uparrow(\downarrow)L L'}^{\alpha \rho, n} = & - \int d\mathbf{r}_i Z_{\uparrow(\downarrow)L}^{\alpha}(\mathbf{r}_i) \left[ \int d\mathbf{r}'_i \frac{f_n(\mathbf{r}'_i)}{|\mathbf{r}_i - \mathbf{r}'_i|} \right. \\ & \left. + \left( \frac{d v_{xc}(\mathbf{r}_i)}{d \rho_{\alpha}} + (-) \frac{d v_{xc}(\mathbf{r}_i)}{d \rho_{\alpha}} \right) f_n(\mathbf{r}_i) \right] Z_{\uparrow(\downarrow)L'}^{\alpha}(\mathbf{r}_i) \end{aligned} \quad (B12)$$

$$\zeta_{\text{mag}, L_1 \times L_2}^{\alpha, m} = X_{L_1 L_2}^{\alpha, \uparrow} - X_{L_1 L_2}^{\alpha, \downarrow} \quad (B13)$$

$$\zeta_{\text{mag}, L_1 \times L_2}^{\alpha, \mu} = c_{\alpha} \sum_{L_3, L_4} \left[ D_{L_1 L_3}^{\alpha, \uparrow} U_{\uparrow L_3, L_4}^{\alpha, \mu} D_{L_4 L_2}^{\alpha, \uparrow} - D_{L_1 L_3}^{\alpha, \downarrow} U_{\downarrow L_3, L_4}^{\alpha, \mu} D_{L_4 L_2}^{\alpha, \downarrow} \right] \quad (B14)$$

$$\begin{aligned} \zeta_{L_1 \times L_2}^{P(H)} = & (-) \sum_{L_3, L_4} [c(D_{L_1 L_3}^{A, \uparrow} F_{\uparrow L_3, L_4}^{A, 1} D_{L_4 L_2}^{A, \uparrow} + D_{L_1 L_3}^{A, \downarrow} F_{\downarrow L_3, L_4}^{A, 1} D_{L_4 L_2}^{A, \downarrow})(1-c) \\ & \times (D_{L_1 L_3}^{B, \uparrow} F_{\uparrow L_3, L_4}^{B, 1} D_{L_4 L_2}^{B, \uparrow} + D_{L_1 L_3}^{B, \downarrow} F_{\downarrow L_3, L_4}^{B, 1} D_{L_4 L_2}^{B, \downarrow})] \end{aligned} \quad (B15)$$

$$\zeta_{L_1 \times L_2}^c = X_{L_1 L_2}^{A, \uparrow} + X_{L_1 L_2}^{A, \downarrow} - X_{L_1 L_2}^{B, \uparrow} - X_{L_1 L_2}^{B, \downarrow} \quad (B16)$$

$$\zeta_{\text{conc}, L_1 \times L_2}^{\alpha, \rho, n} = c_{\alpha} \sum_{L_3, L_4} [D_{L_1 L_3}^{\alpha, \uparrow} U_{\uparrow L_3, L_4}^{\alpha, \rho, n} D_{L_4 L_2}^{\alpha, \uparrow} + D_{L_1 L_3}^{\alpha, \downarrow} U_{\downarrow L_3, L_4}^{\alpha, \rho, n} D_{L_4 L_2}^{\alpha, \downarrow}] \quad (B17)$$

$$\zeta_{\text{conc}, L_1 \times L_2}^{\alpha, \mu} = c_{\alpha} \sum_{L_3, L_4} [D_{L_1 L_3}^{\alpha, \uparrow} U_{\uparrow L_3, L_4}^{\alpha, \mu} D_{L_4 L_2}^{\alpha, \uparrow} + D_{L_1 L_3}^{\alpha, \downarrow} U_{\downarrow L_3, L_4}^{\alpha, \mu} D_{L_4 L_2}^{\alpha, \downarrow}] \quad (B18)$$

where  $c_A = c$  and  $c_B = 1 - c$ . We can now spell out explicitly the key terms. Firstly, part of the chemical interchange energy

$$S^{cc}(\mathbf{q}) = \frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} \left( (D^{A,\uparrow} + D^{A,\downarrow} - D^{B,\uparrow} - D^{B,\downarrow})(\tau_0^{c,00})^{-1} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^c \quad (\text{B19})$$

is the entire contribution when 'band-energy' only effects are considered, i.e., we ignore all charge rearrangement effects. It is the generalization to a DLM paramagnetic alloy of the direct correlation function of Gyorffy and Stocks who considered Fermi surface and band-filling (or  $e/a$ ) effects only [27]. The remaining terms can be expressed in a similar way.

$$J_{\alpha\beta}^{mm}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} \left( (D^{\alpha,\uparrow} - D^{\alpha,\downarrow})(\tau_0^{c,00})^{-1} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{mag}, L_1 \times L_2}^{\beta, m} \quad (\text{B20})$$

$$J_{\alpha\beta}^{\mu\mu}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha,1} D^{\alpha,\uparrow} D^{\alpha,\uparrow} + F_{\downarrow}^{\alpha,1} D^{\alpha,\downarrow} D^{\alpha,\downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{mag}, L_1 \times L_2}^{\beta, m} \quad (\text{B21})$$

$$\Sigma_{\alpha}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} \left( (D^{\alpha,\uparrow} - D^{\alpha,\downarrow})(\tau_0^{c,00})^{-1} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{L_1 \times L_2}^H \quad (\text{B22})$$

$$\chi_{\alpha}^0(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha,1} D^{\alpha,\uparrow} D^{\alpha,\uparrow} + F_{\downarrow}^{\alpha,1} D^{\alpha,\downarrow} D^{\alpha,\downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{L_1 \times L_2}^H \quad (\text{B23})$$

$$\gamma_{\alpha\beta}^{\mu\mu}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha,1} D^{\alpha,\uparrow} D^{\alpha,\uparrow} + F_{\downarrow}^{\alpha,1} D^{\alpha,\downarrow} D^{\alpha,\downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{mag}, L_1 \times L_2}^{\beta, \mu} \quad (\text{B24})$$

$$\gamma_{\alpha\beta}^{\mu m}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} \left( (D^{\alpha,\uparrow} - D^{\alpha,\downarrow})(\tau_0^{c,00})^{-1} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{mag}, L_1 \times L_2}^{\beta, \mu} \quad (\text{B25})$$

$$S_{\alpha}^{cp,n}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon - \mu) \sum_{LL'} \left( (D^{A,\uparrow} + D^{A,\downarrow} - D^{B,\uparrow} - D^{B,\downarrow})(\tau_0^{c,00})^{-1} \right)_{LL'}$$

$$\times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\alpha, \rho, n} \quad (\text{B26})$$

$$S_{\alpha}^{\mu, n}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} \left( (D^{\text{A}, \uparrow} + D^{\text{A}, \downarrow} - D^{\text{B}, \uparrow} - D^{\text{B}, \downarrow}) (\tau_0^{\text{c}, 00})^{-1} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\alpha, \mu, n} \quad (\text{B27})$$

$$S^{\text{cP}}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} \left( (D^{\text{A}, \uparrow} + D^{\text{A}, \downarrow} - D^{\text{B}, \uparrow} - D^{\text{B}, \downarrow}) (\tau_0^{\text{c}, 00})^{-1} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{L_1 \times L_2}^{\text{P}} \quad (\text{B28})$$

$$\epsilon_{\alpha}^{\rho(\mu)\text{c}; n'}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} + (-) F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\text{c}} \quad (\text{B29})$$

$$\epsilon_{\alpha}^{\rho\text{P}; n'}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} + F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{L_1 \times L_2}^{\text{P}} + \frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \int d\mathbf{r}_i f_{n'}(\mathbf{r}_i) \int d\mathbf{r}'_i \\ \times (G^{\alpha, \uparrow}(\mathbf{r}_i, \mathbf{r}'_i) G^{\alpha, \uparrow}(\mathbf{r}'_i, \mathbf{r}_i) + G^{\alpha, \downarrow}(\mathbf{r}_i, \mathbf{r}'_i) G^{\alpha, \downarrow}(\mathbf{r}'_i, \mathbf{r}_i)) \quad (\text{B30})$$

$$\epsilon_{\alpha}^{\mu\text{P}; n'}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} - F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{L_1 \times L_2}^{\text{P}} \quad (\text{B31})$$

$$\epsilon_{\alpha\beta}^{\rho\rho; n'n}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} + F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\beta, \rho, n} \\ - \delta_{\alpha\beta} \frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \int d\mathbf{r}_i f_{n'}(\mathbf{r}_i) \int d\mathbf{r}'_i (G^{\beta, \uparrow}(\mathbf{r}_i, \mathbf{r}'_i) + G^{\beta, \downarrow}(\mathbf{r}_i, \mathbf{r}'_i)) \\ \times \int d\mathbf{r}_i^* \left[ \frac{f_n(\mathbf{r}_i^*)}{|\mathbf{r}_i' - \mathbf{r}_i^*|} + \frac{d\nu_{\text{xc}}}{d\rho^{\beta}(\mathbf{r}_i')} f_n((\mathbf{r}_i')) \right] (G^{\beta, \uparrow}(\mathbf{r}_i', \mathbf{r}_i) + G^{\beta, \downarrow}(\mathbf{r}_i', \mathbf{r}_i)) \quad (\text{B32})$$

$$\epsilon_{\alpha\beta}^{\rho\mu}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} - F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'} \\ \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\beta, \rho, 1} \quad (\text{B33})$$

$$\epsilon_{\alpha\beta}^{\mu\rho}(\mathbf{q}) = -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} + F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'}$$

$$\begin{aligned} & \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\beta, \mu, 1} \\ & - \delta_{\alpha\beta} \frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \int d\mathbf{r}_i f_{n'}(\mathbf{r}_i) \int d\mathbf{r}'_i (G^{\beta, \uparrow}(\mathbf{r}_i, \mathbf{r}'_i) + G^{\beta, \downarrow}(\mathbf{r}_i, \mathbf{r}'_i)) \\ & \times \int d\mathbf{r}'_i \left[ \frac{f_n(\mathbf{r}'_i)}{|\mathbf{r}'_i - \mathbf{r}_i^*|} + \frac{dv_{xc}}{d\rho^\beta(\mathbf{r}'_i)} f_n(\mathbf{r}'_i) \right] (G^{\beta, \uparrow}(\mathbf{r}'_i, \mathbf{r}_i) + G^{\beta, \downarrow}(\mathbf{r}'_i, \mathbf{r}_i)) \end{aligned} \quad (\text{B34})$$

$$\begin{aligned} \epsilon_{\alpha\beta}^{\mu\mu}(\mathbf{q}) = & -\frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon - \mu) \sum_{LL'} u_1 \left( F_{\uparrow}^{\alpha, n'} D^{\alpha, \uparrow} D^{\alpha, \uparrow} - F_{\downarrow}^{\alpha, n'} D^{\alpha, \downarrow} D^{\alpha, \downarrow} \right)_{LL'} \\ & \times \sum_{L_1 \times L_2} T_{L \times L', L_1 \times L_2}(\mathbf{q}) \lambda_{\text{conc}, L_1 \times L_2}^{\beta, \mu, 1} \end{aligned} \quad (\text{B35})$$

## References

- [1] Ling M F, Staunton J B and Johnson D D 1994 *J. Phys.: Condens. Matter* submitted
- [2] Moriya T (ed) 1981 *Electronic Correlations and Magnetism in Narrow Band Systems* (Berlin: Springer)
- [3] Murata K K and Doniach S 1972 *Phys. Rev. Lett.* **29** 285
- [4] Moriya T and Kawabata A 1973 *J. Phys. Soc. Japan* **34** 639
- [5] Lonzarich G G and Taillefer L 1985 *J. Phys. C: Solid State Phys.* **18** 4339
- [6] Korenman V, Murray J L and Prange R E 1977 *Phys. Rev. B* **16** 4032, 4048, 4058
- [7] Ziebeck K R A and Brown P J 1980 *J. Phys. F: Met. Phys.* **10** 2015  
Ziebeck K R A, Brown P J, Deportes J, Givord D, Webster P J and Booth J G 1983 *Proc. 3rd Gen. Conf. Condens. Matter Division EPS; Helv. Phys. Acta* **56** 117
- [8] Shirane G 1984 *J. Magn. Magn. Mater.* **45** 33  
Shirane G, Boni P and Wicksted J 1986 *Phys. Rev. B* **33** 1881
- [9] Edwards D M 1984 *J. Magn. Magn. Mater.* **45** 151
- [10] Hubbard J 1979 *Phys. Rev. B* **20** 4584
- [11] Hasegawa H 1979 *J. Phys. Soc. Japan* **46** 1504
- [12] Hasegawa H 1981 *J. Phys. Soc. Japan* **51** 802
- [13] Gyorffy B L, Pindor A J, Staunton J B, Stocks G M and Winter H 1985 *J. Phys. F: Met. Phys.* **15** 1337
- [14] Pindor A J, Staunton J B, Stocks G M and Winter H 1983 *J. Phys. F: Met. Phys.* **13** 979
- [15] Staunton J B, Gyorffy B L, Pindor A J, Stocks G M and Winter H 1985 *J. Phys. F: Met. Phys.* **15** 1387
- [16] Heine V and Joynt R 1988 *Europhys. Lett.* **5** 81
- [17] Samson J 1989 *J. Phys.: Condens. Matter* **1** 6717
- [18] Luchini M U and Heine V 1991 *Europhys. Lett.* **14** 609
- [19] Chana K S, Samson J H, Luchini M U and Heine V 1991 *J. Phys.: Condens. Matter* **3** 6455
- [20] Staunton J B, Gyorffy B L, Stocks G M and Wadsworth J 1986 *J. Phys. F: Met. Phys.* **16** 1761
- [21] Sandratskii L M and Kubler J 1992 *J. Phys.: Condens. Matter* **4** 6927
- [22] Staunton J B and Gyorffy B L 1992 *Phys. Rev. Lett.* **69** 371
- [23] Mermin N D 1965 *Phys. Rev.* **137** A1441
- [24] Feynman R P 1955 *Phys. Rev.* **97** 660
- [25] Soven P 1967 *Phys. Rev.* **156** 809
- [26] Gautier F, Ducastelle F and Giner J 1975 *Phil. Mag.* **31** 1373
- [27] Gyorffy B L and Stocks G M 1983 *Phys. Rev. Lett.* **50** 374
- [28] Stocks G M and Winter H 1982 *Z. Phys. B* **46** 95
- [29] Johnson D D, Nicholson D M, Pinski F J, Gyorffy B L and Stocks G M 1986 *Phys. Rev. Lett.* **56** 2088;  
1990 *Phys. Rev. B* **41**, 9701
- [30] Haines E, Clauberg R and Feder R 1985 *Phys. Rev. Lett.* **54** 932
- [31] Faulkner J S and Stocks G M 1980 *Phys. Rev. B* **21** 3222
- [32] Gyorffy B L and Stott M J 1972 *Band Structure Spectroscopy of Metals and Alloys* ed D J Fabian and L M Watson (New York: Academic)
- [33] Brout R and Thomas H 1967 *Physica* **3** 317

- [34] Gyorffy B L, Johnson D D, Pinski F J, Nicholson D M and Stocks D M 1989 *Alloy Phase Stability, NATO-ASI Series E163* ed G M Stocks and A Gonis (Dordrecht: Kluwer) pp 421–68  
Stocks G M et al 1993 *Statics and Dynamics of Alloy Phase Transformations, NATO-ASI Series* ed A Gonis and P E A Turchi (New York: Plenum)
- [35] Ducastelle F et al 1989 *Alloy Phase Stability, NATO-ASI Series E163* ed G M Stocks and A Gonis (Dordrecht: Kluwer) pp 293–328
- [36] de Fontaine D et al 1989 *Alloy Phase Stability, NATO-ASI Series E163* ed G M Stocks and A Gonis (Dordrecht: Kluwer) pp 177–204
- [37] Connolly J W D and Williams A R 1983 *Phys. Rev. B* **27** 5169
- [38] Zunger A 1993 *Statics and Dynamics of Alloy Phase Transformations, NATO-ASI Series* ed A Gonis and P E A Turchi (New York: Plenum)
- [39] Zunger A 1991 *Structural and Phase Stability of Alloys* ed J L Moran-Lopez, F Mejialira and J M Sanchez (New York: Plenum) ch 17
- [40] Khachatryan A G 1983 *Theory of Structural Transformations in Solids* (New York: Wiley and Sons) p 39
- [41] Staunton J B, Johnson D D and Pinski F J 1994 *Phys. Rev. B* submitted
- [42] Johnson D D, Staunton J B and Pinski F J 1994 *Phys. Rev. B* submitted
- [43] Ducastelle F and Gautier F 1976 *J. Phys. F: Met. Phys.* **6** 2039
- [44] Staunton J B, Johnson D D and Gyorffy B L 1994 *J. Appl. Phys.* **61** 3693  
Ling M F, Staunton J B and Johnson D D in preparation
- [45] Gorsky V B 1928 *Z. Phys.* **50** 64  
Bragg W L and Williams E J 1934 *Proc. R. Soc. A* **145** 699; 1935 *Proc. R. Soc. A* **152** 231
- [46] Gunnarsson O 1976 *J. Phys. F: Met. Phys.* **6** 587
- [47] Pettifor D G 1978 *Solid State Commun.* **28** 621; 1979 *Phys. Rev. Lett.* **42** 846