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Nonsite diagonal properties from the Korringa-Kohn-Rostocker nonlocal coherent-potential approximation

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We present a formalism for the Bloch spectral function within the framework of the recently devised Korringa-Kohn-Rostocker nonlocal coherent potential approximation (KKR-NLCPA). This is applicable to the study of the effects of short-range order (SRO) on the electronic structure of disordered systems. We show how a coarse-grained average of the spectral function over regions in reciprocal space results directly from the KKR-NLCPA. By considering fluctuations about the NLCPA effective medium we find an expression for the spectral function itself. The results of explicit calculations on the bcc $Cu_{50}Zn_{50}$ and the fcc $Cu_{77}Ni_{23}$ solid solutions are presented in order to examine the effects of SRO upon their electronic structure and to illustrate the validity of our formalism.

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I. INTRODUCTION

Over the past 30 years, effective medium theories have proven to be of great utility in the study of substitutionally disordered crystals[1,2] such as metallic alloys. In contrast to conventional electronic structure theory techniques, whereby one has to calculate the electronic structure of each configuration and then average over these configurations to obtain physical properties, the effective medium is constructed so as to describe the ensemble average over all alloy configurations. As a translationally invariant quantity, it permits the familiar arsenal of techniques from the analysis of crystalline systems such as lattice Fourier transforms to be applied without recourse to the use of computationally expensive supercells. The natural description of the effective medium is provided by multiple scattering theory; effective scattering amplitudes $\hat{t}$ are located on each lattice site and structure constants $\hat{G}$ then describe the propagation of an electron through the configurationally averaged lattice, whilst the medium itself may be determined via a physically reasonable and intuitive self-consistency condition.

One well-known means of determining the effective medium is provided by the the so-called coherent potential approximation (CPA),[3] which represents the state-of-the-art method for describing the electronic structure of disordered metals.[4,5] In conjunction with density functional theory (DFT)[6,7] and the Korringa-Kohn-Rostocker (KKR) method of band theory,[8–10] it is capable of providing an accurate *ab initio* description of such systems, as a long history of successful applications testifies.[2,11–13] At its heart, though, the KKR-CPA remains a single-site mean-field theory,[14] and it is thus incapable of dealing with short-range order (SRO) effects, viz. the fluctuations in the crystal potential arising from the disorder in the environment of each site. It therefore explicitly ignores the role that SRO may play in the physics of such systems. Such statistical fluctuations are responsible for band tailing and sharp structure in densities of states;[1] the neglect of them yields **k**-independent momentum-state lifetimes. A single-site theory is further incapable of rigorously treating transport properties and the localization of states.[1] The effects of SRO upon the electronic structure of disordered alloys have been examined by Mookerjee and Prasad,[15–17] using a TB-LMTO (tight-binding linear muffin-tin orbital) method[18] in conjunction with an augmented space formalism[19,20] and real space recursion method,[21] whilst Saha *et al.*[22] have obtained spectral functions within the same framework. However, it is useful to be able to examine such effects within a computationally tractable extension of the KKR-CPA.

These considerations have motivated the recent work of Rowlands *et al.*,[23–25] along with Biava *et al.*[26] References 23 and 24 formulate and illustrate a successful method incorporating the effects of SRO within the framework of KKR-CPA theory, whilst implementation for realistic systems is described in Refs. 25 and 26. This nonlocal CPA (NLCPA) theory is based upon reciprocal space coarse-graining ideas introduced by Jarrell and Krishnamurthy[27] originating from the dynamical cluster approximation (DCA).[28–30] The KKR-NLCPA[24,25] introduces an effective (translationally invariant) disorder term δG which represents an effective propagator that accounts for all nonlocal scattering correlations on the electronic propagation due to disorder configurations and modifies the structure constants accordingly. By coarse-graining reciprocal space, one naturally introduces real space periodically repeating clusters. As such, the NLCPA maps an effective lattice problem to that of an impurity cluster embedded in a self-consistently determined effective medium, and thus yields a cluster generalization of the KKR-CPA that includes nonlocal correlations up to the range of the cluster size. Unlike other cluster approaches, such as the molecular CPA (MCPA)[31] it is fully translationally invariant, that is, the effective medium has the site-to-site translational invariance of the underlying lattice. It is also computationally tractable, largely on account of the reciprocal space coarse-graining procedure employed.

Our purpose in this paper is to focus on the calculation of observable quantities using the KKR-NLCPA. Rowlands *et al.*[23,24] demonstrated explicitly how to obtain site-diagonal observable properties such as the total and component densities of states, whilst in Ref. 25, the same authors showed that such quantities could be calculated for realistic systems such as the CuZn solid solution examined therein. However, as we show here, it can also be used to calculate so-called non-site-diagonal properties such as the Bloch spectral function.

For a perfectly periodic solid, the spectral function can be written

$$A_b(E,\mathbf{k}) = \sum_n \delta[E - E_n(\mathbf{k})] \tag{1}$$

where the $E_n(\mathbf{k})$ are band structure eigenvalues. As can be seen, for a given k point, this will consist of infinitesimally sharp peaks at these corresponding band energies, and will be zero for all other energies, whilst integrating over the Brillouin zone yields the density of states.

The effects of disorder will be to broaden these peaks; the half-width of which is related to the lifetime of an electron in a state $\mathbf{k}$. Experimentally, these lifetimes can be determined by positron annihilation experiments,[32] or through angle-resolved photoemission measurements.[33,34] As a density of states in reciprocal space, the Bloch spectral function yields valuable information on the Fermi surface of disordered alloys; calculating this quantity within the NLCPA therefore allows the effects of SRO on, for example, the Fermi surface topology to be investigated.

For a disordered system the spectral function is connected to the nonsite diagonal, configuration averaged Green's function, $\langle G(E,\mathbf{r},\mathbf{r}')\rangle$, through the Fourier transform

$$A_b(E,\mathbf{k}) = -(1/\pi)\mathrm{Im}\sum_j \int_{\Omega_i} d\mathbf{r}_i \langle G(E,\mathbf{r}_i,\mathbf{r}_i+\mathbf{R}_j)\rangle e^{-i\mathbf{k}\cdot\mathbf{R}_j} \tag{2}$$

where the $\mathbf{R}_j$ denote sites on the lattice, the sum is over all sites within the lattice under consideration, and the integral is taken over the volume of the unit cell surrounding site i.

To this end, we discuss the nonsite diagonal configurationally averaged Green's function, and, taking due care with the lattice Fourier transform involved, use this to derive an explicit expression for the Bloch spectral function. The paper is structured as follows: Sec. II provides a brief overview of the KKR-NLCPA method, and the coarse-graining procedure and demonstrates how this naturally leads to an expression for an average of the spectral function over a reciprocal space tile; in Sec. III we describe how to calculate the spectral function at selected reciprocal space points; in Sec. IV we evaluate this quantity to investigate the effects of SRO electronic structure of the bcc $\mathrm{Cu}_{50}\mathrm{Zn}_{50}$ alloy. In Sec. V we discuss how to obtain the spectral function for any point in the Brillouin zone, and illustrate this by examining the effects of SRO upon the electronic structure of the fcc $\mathrm{Cu}_{77}\mathrm{Ni}_{23}$ alloy. In Sec. VI we present our conclusions.

II. KKR-NLCPA: AN OVERVIEW

The first step in the KKR-NLCPA is to define the NLCPA effective medium.[24,25] The propagation of an electron through this medium is described by the scattering path matrix $\hat{\underline{\tau}}^{ij}$, which should be determined such that it describes the motion of an electron on the average exactly. We define it through

$$\hat{\underline{\tau}}^{ij} = \hat{\underline{\tau}}\delta_{ij} + \sum_{k\neq i} \hat{\underline{t}}\hat{\underline{G}}(\mathbf{R}_{ik})\hat{\underline{\tau}}^{kj} \tag{3}$$

where a circumflex symbol denotes an effective medium quantity, and an underscore denotes a matrix in angular momentum and cluster space. The effective local t matrices (i.e., the scattering amplitudes) are defined $\hat{\underline{t}}$, and the effective propagator is given by

$$\hat{\underline{G}}(\mathbf{R}_{ij}) = \underline{G}(\mathbf{R}_{ij}) + \underline{\delta\hat{G}}(\mathbf{R}_{ij}), \tag{4}$$

where we have the usual free-space KKR structure constants $\underline{G}(\mathbf{R}_{ij})$ that account for the lattice structure, and have introduced the translationally invariant screening term, $\underline{\delta\hat{G}}(\mathbf{R}_{ij})$. This modifies the free-space KKR structure constants, and as explained by Rowlands *et al.*,[24,25] accounts, in an averaged manner, for all nonlocal scattering correlations due to the disorder configurations. Invoking translational invariance allows us to write the scattering path matrix $\hat{\underline{\tau}}^{ij}$ as follows:

$$\hat{\underline{\tau}}^{ij} = \frac{1}{\Omega_{BZ}}\int_{\Omega_{BZ}} d\mathbf{k}(\hat{\underline{t}}^{-1} - \underline{G}(\mathbf{k}) - \underline{\delta\hat{G}}(\mathbf{k}))^{-1} e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}. \tag{5}$$

It is not feasible to solve this problem exactly; the essential idea, influenced by the work of Jarrell and Krishnamurthy on the dynamical cluster approximation,[27] is to consistently coarse grain in both real and reciprocal space. The coarse-graining algorithm must preserve the translational invariance and point group symmetry of the underlying lattice, and a detailed discussion of the construction employed in this work has been provided by Rowlands *et al.*[24,25] The coarse graining amounts to finding "cluster momenta" and N_c real-space cluster sites satisfying

$$\frac{1}{N_c}\sum_{\mathbf{K}_n} e^{i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)} = \delta_{IJ}, \tag{6}$$

where the $\{\mathbf{K}_n\}$ are at the centers of a set of N_c reciprocal space patches or tiles that coarse grain the first Brillouin zone of the lattice, and the $\{\mathbf{R}_I\}$ define a real-space cluster of N_c sites surrounded by a tile similarly preserving the point-group symmetry, which may be periodically repeated to yield the original lattice.

Having determined the cluster momenta and real space sites consistent with Eq. (6), it is now possible to determine the effective medium. This may be achieved by approximating the $\underline{\delta\hat{G}}(\mathbf{k})$ within each of the N_c tiles in reciprocal space by the N_c values $\{\underline{\delta\hat{G}}(\mathbf{K}_n)\}$, each of which is defined to be the average of $\underline{\delta\hat{G}}(\mathbf{k})$ over the tile centered at $\mathbf{K}_n$. The coarse-grained averaged effective medium path operator may be represented by

$$\underline{\hat{\tau}}(\mathbf{K}_n) = \frac{N_c}{\Omega_{BZ}} \int_{\Omega_{\mathbf{K}_n}} d\tilde{\mathbf{k}} (\underline{\hat{t}}^{-1} - \underline{G}(\mathbf{K}_n + \tilde{\mathbf{k}}) - \underline{\delta\hat{G}}(\mathbf{K}_n))^{-1} \tag{7}$$

which is simple to calculate, as $\underline{\delta\hat{G}}$ is taken to be constant within a given tile with volume $\Omega_{\mathbf{K}_n}$. Here, $\tilde{\mathbf{k}}$ is a reciprocal space point located within the NLCPA reciprocal space tile centered upon $\mathbf{K}_n$, and a point in reciprocal space $\mathbf{k}$ may accordingly be written

$$\mathbf{k} = \mathbf{K}_n + \tilde{\mathbf{k}}. \tag{8}$$

These integrals have the same computational cost as a standard BZ integration; it is this that renders the NLCPA computationally inexpensive, in marked contrast to earlier cluster theories such as MCPA.[1,24] Defining Fourier transforms through

$$\underline{\hat{\tau}}^{IJ} = 1/N_c \sum_{\mathbf{K}_n} \underline{\hat{\tau}}(\mathbf{K}_n) e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} \tag{9}$$

and

$$\underline{\hat{\tau}}(\mathbf{K}_n) = \sum_J \underline{\hat{\tau}}^{IJ} e^{-i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} \tag{10}$$

the corresponding expression for the path scattering operator between cluster sites is

$$\underline{\hat{\tau}}^{IJ} = \frac{1}{\Omega_{BZ}} \sum_{\mathbf{K}_n} \left(\int_{\Omega_{\mathbf{K}_n}} d\tilde{\mathbf{k}} [\underline{\hat{t}}^{-1} - \underline{G}(\mathbf{K}_n + \tilde{\mathbf{k}}) - \underline{\delta\hat{G}}(\mathbf{K}_n)]^{-1} \right) \times e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)}. \tag{11}$$

Nyquist's sampling theorem[35] implies that coarse-graining the effective structure constant corrections has the effect of reducing their range in real space. Using Eq. (6) we can thus write

$$\underline{\delta\hat{G}}^{IJ} = \frac{1}{N_c} \sum_{\mathbf{K}_n} \underline{\delta\hat{G}}(\mathbf{K}_n) e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)}, \tag{12}$$

$$\underline{\delta\hat{G}}(\mathbf{K}_n) = \sum_{J \neq I} \underline{\delta\hat{G}}^{IJ} e^{-i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} \tag{13}$$

from which it is apparent that $\underline{\delta\hat{G}}(\mathbf{R}_{ij})$ remains translationally invariant and only dependent upon the distance between sites I and J. It is therefore independent of which site in the lattice is chosen to be site I. Note further that it is now restricted to act within the NLCPA cluster. It is straightforward to now extend the CPA arguments, as in Refs. 23 and 24, and embed an impurity cluster (chosen so as to satisfy the above requirements) into the effective medium. By considering all possible paths starting and ending on the impurity cluster sites and demanding that, on the average, there is no excess scattering off the embedded cluster, which may be expressed as

$$\sum_\gamma P(\gamma) \underline{\tau}^{IJ}_\gamma = \underline{\hat{\tau}}^{IJ} \tag{14}$$

the effective medium may be determined. Here, $P(\gamma)$ is the probability of configuration γ occurring, and for a binary alloy, the sum is over the 2^{N_c} possible impurity configurations, and $\underline{\tau}^{IJ}_\gamma$ is the scattering path matrix from cluster site I to J, for a given cluster configuration γ. The effective medium may therefore be determined through a self-consistent solution of Eqs. (11) and (14) We may include SRO by appropriately weighting configurations. A detailed discussion of the self-consistent algorithm used in this work is provided in Refs. 23 and 24

A. Calculation of observables

The calculation of physical observables proceeds from determination of the configuration average of the Green's function. In general, the multiple-scattering Green's function may be written (Ref. 36)

$$G(E, \mathbf{r}_i, \mathbf{r}'_j) = \sum_{LL'} Z^i_L(E, \mathbf{r}_i) \tau^{ij}_{LL'} Z^j_{L'}(E, \mathbf{r}'_j) - \sum_L Z^i_L(E, \mathbf{r}_i) J^i_L(E, \mathbf{r}'_i) \delta_{ij}, \tag{15}$$

where the $L(=l, m)$ is an angular momentum label, and $\mathbf{r}_i(\mathbf{r}_j)$ lies within the unit cell centered upon site $i(j)$. The Z_L and J_L denote the regular and irregular solutions to the Schrödinger equation, respectively. The site-diagonal Green's function, configurationally averaged such that the potential at site I is fixed, is given by

$$\langle G(E, \mathbf{r}_I, \mathbf{r}'_I) \rangle_I = \sum_\gamma P(\gamma|I) \sum_{L,L'} Z^I_L(E, \mathbf{r}_I) \langle \tau^{II}_{LL'} \rangle_{I;\gamma} Z^I_{L'}(E, \mathbf{r}'_I) - \delta_{LL'} \sum_L Z^I_L(E, \mathbf{r}_I) J^I_{L'}(E, \mathbf{r}'_I). \tag{16}$$

Here, $\langle \tau^{II}_{LL'} \rangle_{I;\gamma}$ is the path scattering operator for paths starting and ending at site I, conditionally averaged such that the potential on site I is known, and the rest of the sites are described by configuration γ. $P(\gamma|I)$ is then the probability of configuration γ occurring, given the potential at site I. Averaging over the occupants of this site then yields

$$\langle G(E, \mathbf{r}_I, \mathbf{r}'_I) \rangle = \sum_\alpha P(\alpha|I) \left(\sum_\gamma P(\gamma|\alpha) \sum_{L,L'} Z^I_L(E, \mathbf{r}_I) \times \langle \tau^{II}_{LL'} \rangle_{I;\gamma} Z^I_{L'}(E, \mathbf{r}'_I) - \delta_{LL'} \sum_L Z^I_L(E, \mathbf{r}_I) J^I_{L'}(E, \mathbf{r}'_I) \right), \tag{17}$$

where the index α may be either of type A or B for a binary alloy A_cB_{1-c}, and $P(\alpha|I)$ is the probability that site I is occupied by an atom of type α.

Translational invariance implies that any site may be chosen to be site I, and accordingly, the density of states is given by

$$\rho(E) = \frac{-1}{\pi} \,\mathrm{Im} \int_{\Omega_I} \langle G(E,\mathbf{r}_I,\mathbf{r}_I) \rangle d\mathbf{r}_I, \tag{18}$$

where the integral is taken over Ω_I, the volume of site I.

B. Coarse grained Bloch spectral function

We now focus attention on the nonsite diagonal configuration averaged Green's function for sites I,J within the same NLCPA cluster, i.e.,

$$\begin{aligned}\langle G(E,\mathbf{r}_I,\mathbf{r}'_J)\rangle_{IJ} = \sum_{\gamma} P(\gamma|IJ) \sum_{L,L'} Z^I_L(E,\mathbf{r}_I) \\ \times \langle \tau^{IJ}_{LL'} \rangle_{I,J;\gamma} Z^J_{L'}(E,\mathbf{r}'_J) \\ - \delta_{IJ} \sum_L Z^I_L(E,\mathbf{r}_I) J^I_L(E,\mathbf{r}'_J)\end{aligned} \tag{19}$$

which is a straightforward extension of the site-diagonal expression given by Rowlands *et al.*[24] Analogous to the site-diagonal case, $\langle \tau^{IJ}_{LL'} \rangle_{I,J;\gamma}$ is the path scattering operator from site I to site J, conditionally averaged such that the occupancies of these two sites are known. $P(\gamma|IJ)$ is then the probability that the remainder of the cluster sites are occupied in accordance with configuration γ, given the specification of the occupancies of sites I and J.

Averaging over all possible occupancies of the two sites then yields an expression for $\langle G(E,\mathbf{r}_I,\mathbf{r}'_J)\rangle$:

$$\begin{aligned}\langle G(E,\mathbf{r}_I,\mathbf{r}'_J)\rangle = \sum_{\alpha\beta} P(\alpha,\beta|IJ) \Biggl(\sum_{\gamma} P(\gamma|\alpha\beta) \sum_{L,L'} Z^\alpha_L(E,\mathbf{r}_I) \\ \times \langle \tau^{IJ}_{LL'} \rangle_{\alpha,\beta;\gamma} Z^\beta_{L'}(E,\mathbf{r}'_J) \\ - \delta_{IJ}\delta_{\alpha\beta} \sum_L Z^\alpha_L(E,\mathbf{r}_I) J^\beta_L(E,\mathbf{r}'_J) \Biggr),\end{aligned} \tag{20}$$

where $\alpha\beta$ may take the values AA, AB, BA, BB, for a binary alloy. Here, the path scattering operator may be written as

$$\langle \tau^{IJ}_{LL'} \rangle_{\alpha,\beta;\gamma} = (\hat{\underline{\tau}}^{-1} + \underline{t}^{-1}(\alpha,\beta;\gamma) - \hat{\underline{t}}^{-1} + \underline{\delta\hat{G}})^{-1}_{I,J,L,L'} \tag{21}$$

with $\underline{t}^{-1}(\alpha,\beta;\gamma)$ denoting a set of scatterers comprising the cluster such that for configuration γ, site I is occupied by an α atom and site J by a β atom. This expression for the averaged Green's function is valid for all sites separated by distances less than the extent of the cluster.

If we now coarse grain the KKR-NLCPA Green's function consistently with Eq. (6), i.e., Fourier transform this quantity at the cluster momenta, we obtain the following:

$$\begin{aligned}\bar{A}_b(E,\mathbf{K}_n) = -(1/N_c\pi)\mathrm{Im} \sum_J \Biggl(\sum_{\alpha\beta} P(\alpha\beta|IJ) \\ \times \sum_\gamma P(\gamma|\alpha\beta) \sum_{LL'} (F^{\alpha\beta}_{LL'} \langle \tau^{IJ}_{LL'} \rangle_{\alpha\beta;\gamma} \\ - \delta_{LL'}\delta_{\alpha\beta} \bar{F}^\alpha_{LL'}) \Biggr) e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I - \mathbf{R}_J)},\end{aligned} \tag{22}$$

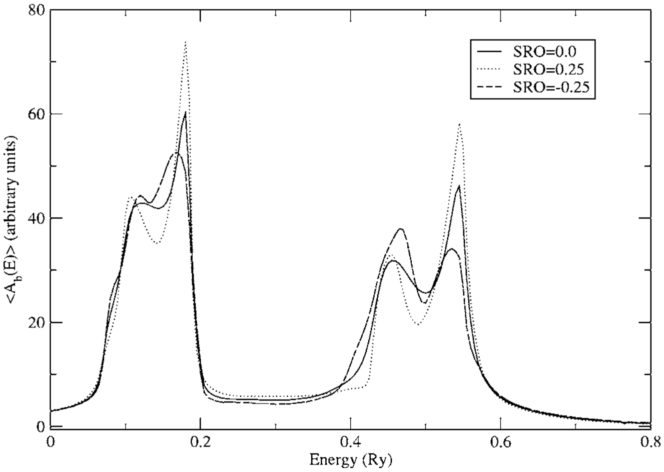

FIG. 1. Coarse-grain averaged spectral fuanction over the NLCPA tile centered at Brillouin zone origin.

which is a well-defined quantity within the NLCPA. The matrix $\underline{F}^{\alpha\beta}$ is given by

$$F^{\alpha\beta}_{LL'} = \int_{\Omega_I} Z^\alpha_L(E,\mathbf{r}_I) Z^\beta_{L'}(E,\mathbf{r}_I) d\mathbf{r}_I, \tag{23}$$

and the matrix $\underline{\bar{F}}^\alpha$ is given by

$$\bar{F}^\alpha_{LL'} = \int_{\Omega_I} Z^\alpha_L(E,\mathbf{r}_I) J^\alpha_{L'}(E,\mathbf{r}_I) d\mathbf{r}_I, \tag{24}$$

where the integrals in each case are taken over the volume of site I. In the expression for $\underline{F}^{\alpha\beta}$, we have implicitly used the periodicity of the lattice to permit us to integrate over the volume of site I.

As can be seen, this quantity naturally arises from the KKR-NLCPA, and corresponds to a coarse-grained average of the Bloch spectral function over the extent of a reciprocal space tile centered on $\mathbf{K}_n$, i.e.,

$$\bar{A}_b(E,\mathbf{K}_n) = \frac{N_c}{N} \sum_{\tilde{\mathbf{k}}} A_b(E,\mathbf{K}_n + \tilde{\mathbf{k}}), \tag{25}$$

where the sum is over $\tilde{\mathbf{k}}$ lying within the tile centered at $\mathbf{K}_n$.

It is easy to see that integrating this over the Brillouin zone satisfies the sum rule

$$\rho(E) = 1/N_c \sum_{\mathbf{K}_n} \bar{A}_b(E,\mathbf{K}_n) \tag{26}$$

where $\rho(E)$ is the density of states.

In Figs. 1 and 2, such coarse-grained averages of the spectral function are presented for bcc CuZn where $N_c = 2$. These results indicate that the coarse-grained spectral function allows us to glean further information on the electronic states; for example, it can be used to identify the regions of reciprocal space responsible for changes observed in the density of states. As an illustration, in Fig. 2, we can see that the shoulder in the density of states at around 0.4 Ry is not only

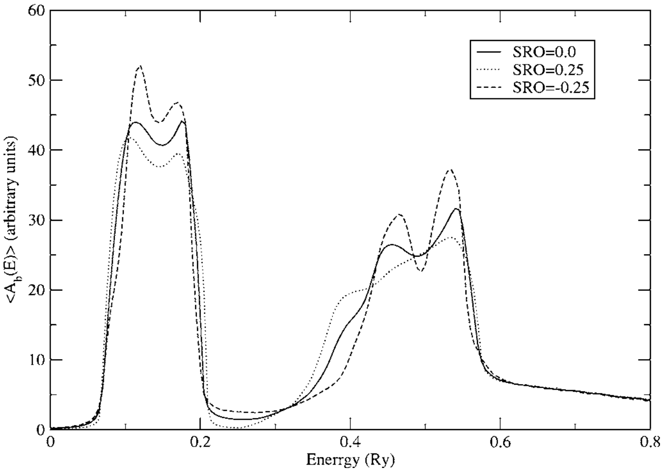

FIG. 2. Coarse-grain averaged spectral function over the NLCPA tile centered at (0,0,1).

enhanced by the clustering tendency, but is also due to states in the reciprocal space tile centered around the point (0,0,1), i.e., towards the edge of the Brillouin zone. Similarly, from Fig. 1, it can be seen that the Cu states responsible for the peaks in the region 0.4–0.6 Ry are located within the tile centered upon the zone center.

It is apparent that in this $N_c=2$ case that the coarse-grained spectral function yields little information about the detailed distribution of the electronic states in reciprocal space. This is to be expected, given its nature as an average over the NLCPA tiles. As such, it provides a "pixellation" of the spectral function across the Brillouin zone, with each tile being a pixel. To improve the resolution of this pixellation demands that the size of the pixels be reduced. This is equivalent to introducing larger clusters into our calculation. Of course, as the limit of an infinite cluster is approached, an exact pixellation is obtained. Given that the number of cluster configurations for a binary alloy is 2^{N_c}, one obvious method to alleviate some computation is to importance sample the configurational phase space. This could take the form of a Monte Carlo scheme with energetic weightings based upon some simple Hamiltonian such as a Bragg-William model. Work is in progress on this development.

III. RECIPROCAL SPACE RESOLUTION

Whilst the information provided by the coarse-grained spectral function is useful, it is desirable to be able to obtain a finer resolution in reciprocal space, i.e., to be able to calculate a spectral function at specific **K** points. To proceed, we note that the Bloch spectral function may be connected to the nonsite diagonal configuration averaged Green's function through Eq. (2), where we must sum over *all* lattice sites in carrying out this Fourier transform. We stress here that this is an important point; simply restricting the sum to cluster sites recovers the coarse grained quantity considered in the previous section. We must now begin to consider in some detail how to carry out this Fourier transform.

A. Configurationally averaged Green's function

The first issue to address is the determination of the configuration averaged Green's function between sites separated by a distance greater than the extent of the cluster. The Green's function may be readily written as

$$G(E,\mathbf{r}_I,\mathbf{r}'_{J'}) = \sum_{L,L'} Z^I_L(E,\mathbf{r}_I)\tau^{IJ'}_{LL'}Z^{J'}_{L}(E,\mathbf{r}'_{J'}), \tag{27}$$

where now, sites I and J' reside in different clusters (a notation that we use throughout in this work). Averaging this expression allows us to write

$$\langle G(E,\mathbf{r}_I,\mathbf{r}'_{J'})\rangle = \sum_{\alpha} P(\alpha|I)\sum_{\alpha'} P(\alpha'|J')\sum_{\gamma} P(\gamma|\alpha)\sum_{\gamma'} P(\gamma'|\alpha')$$
$$\times\sum_{L,L'} Z^{\alpha}_L(E,\mathbf{r}_I)\langle\tau^{IJ'}_{LL'}\rangle_{\alpha;\gamma:\alpha';\gamma'}Z^{\alpha'}_{L'}(E,\mathbf{r}'_{J'}), \tag{28}$$

where $\langle\tau^{IJ'}_{LL'}\rangle_{\alpha;\gamma:\alpha';\gamma'}$ is the path scattering operator from site I to site J', partially averaged such that I resides within a cluster with configuration γ, occupied by atom α and J' resides within a cluster with configuration γ', occupied by atom α', i.e., it is noncluster diagonal quantity describing propagation from a site I in a cluster to a site J' in a different cluster. The NLCPA does not provide a prescription for the calculation of this quantity, and therefore additional assumptions are required. As shown in the Appendix, this average can be carried out by considering fluctuations about the effective medium, yielding the result (where we have suppressed the angular momentum dependence for the sake of clarity)

$$\langle\tau^{IJ'}\rangle_{\alpha;\gamma:\alpha';\gamma'} = \sum_{J,I'} D^{\dagger\alpha;\gamma}_{IJ}\hat{\tau}^{JI'}D^{\alpha';\gamma'}_{I'J'} \tag{29}$$

where the double sum is taken over cluster sites. Here, the matrix $\underline{D}$ is the inverse of the matrix $\underline{M}$, which is given by

$$M^{\alpha;\gamma}_{IJ} = \delta_{IJ} + \sum_{K}[(t^{-1}(\alpha,\gamma) - \hat{t}^{-1})\delta_{IK} + \delta\hat{G}(\mathbf{R}_{IK})]\hat{\tau}^{KJ}, \tag{30}$$

where $t^{-1}(\alpha,\gamma)$ denotes the scattering matrix for a cluster of configuration γ, with an atom of type α on the site I. Equation (29) may be seen as the NLCPA extension of the restricted averages used by Faulkner and Stocks,[36] and the sum over K is taken over NLCPA cluster sites.

B. Lattice Fourier transform of Green's function

We must now Fourier transform the ensemble averaged Green's function. Carrying out this Fourier transform is the KKR-NLCPA extension of Faulkner and Stocks' result for the KKR-CPA.[36] The NLCPA naturally yields well-defined quantities at the cluster momenta $\mathbf{K}_n$; it is accordingly straightforward to calculate a well-defined spectral function at these reciprocal space points.

For convenience, it is possible to split the Fourier transform into two contributions: one from sites that lie within the same cluster as our reference site I; and a second contribution from those sites that lie outside the cluster. We thus write

$$
\begin{aligned}
A_b(E,\mathbf{K}_n) = -(1/N_c\pi)\mathrm{Im}\Bigg(& \sum_J \Bigg\{ \sum_{\alpha\beta} P(\alpha\beta|IJ) \sum_\gamma P(\gamma|\alpha\beta) \sum_{LL'} (F^{\alpha\beta}_{LL'} \langle \tau^{IJ}_{LL'} \rangle_{\alpha\beta;\gamma} - \delta_{LL'}\delta_{\alpha\beta}\bar{F}^{\alpha}_{LL'}) \Bigg\} e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)} \\
& - \sum_J \sum_\alpha \sum_\beta P(\alpha|I)P(\beta|J) \sum_{\gamma,\gamma'} P(\gamma|\alpha)P(\gamma'|\beta) \sum_{LL'} F^{\alpha\beta}_{LL'} \langle \tau^{IJ}_{LL'} \rangle_{\alpha;\gamma:\beta;\gamma'} e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)} \\
& + \sum_j \sum_\alpha \sum_\beta P(\alpha|I)P(\beta|j) \sum_{\gamma,\gamma'} P(\gamma|\alpha)P(\gamma'|\beta) \sum_{LL'} F^{\alpha\beta}_{LL'} \langle \tau^{Ij}_{LL'} \rangle_{\alpha;\gamma:\beta;\gamma'} e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_j)} \Bigg),
\end{aligned} \tag{31}
$$

where the symbols have their usual meanings, and N_c is the number of sites in a cluster. In this expression, the first term is that arising from sites located within the same cluster as the reference site and is equivalent to our coarse-grained Bloch spectral function $\bar{A}_b(E,\mathbf{K}_n)$. We sum over all cluster sites. In our third term, the sum over j is to be taken over *all* sites in the lattice. The second term removes the double counting of the sites within the cluster arising from the sum over all sites j.

At this stage we choose to express $\hat{\tau}^{Ij}$ in terms of its Fourier transform, allowing us to write the third term as follows:

$$
\sum_{\alpha\beta} \sum_j P(\alpha|I)P(\beta|j) \sum_\gamma P(\gamma|\alpha) \sum_{\gamma'} P(\gamma'|\beta) \sum_{LL'} F^{\alpha\beta}_{LL'} \sum_{J_1 I'} \left(D^{\dagger\alpha;\gamma}_{IJ_1} \times 1/\Omega_{BZ} \int_{BZ} \hat{\tau}(\mathbf{k}') e^{i\mathbf{k}'\cdot(\mathbf{R}_{J_1}-\mathbf{R}_{I'})} d\mathbf{k}' D^{\beta;\gamma'}_{I'j} \right)_{LL'} e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_j)}, \tag{32}
$$

where we have used Eq. (29) to express $\langle \tau^{Ij} \rangle$, and the integral is taken over the entire Brillouin zone. We should note too that the sum over cluster sites I' is taken to be over a NLCPA cluster about the site j (i.e., site j is at the origin of such a cluster), whilst that over cluster sites J_1 is taken to be over a NLCPA cluster with site I at the origin.

We can carry out the Fourier transform by writing

$$
\mathbf{R}_{J_1} = \mathbf{R}_I + \mathbf{R}_{J_2}, \tag{33}
$$

where $\mathbf{R}_{J_2}$ denotes the position of a cluster site in a NLCPA cluster about site I at the cluster origin, and

$$
\mathbf{R}_{I'} = \mathbf{R}_j + \mathbf{R}_{I'_1} \tag{34}
$$

where, similarly, $\mathbf{R}_{I'_1}$ denotes the position of a cluster site in a NLCPA cluster about site j at the cluster origin.

Using this, we can write the third term as

$$
\sum_{\alpha\beta} \sum_j P(\alpha|I)P(\beta|j) \sum_\gamma P(\gamma|\alpha) \sum_{\gamma'} P(\gamma'|\beta) \sum_{LL'} F^{\alpha\beta}_{LL'} \sum_{J_1 I'} \left(D^{\dagger\alpha;\gamma}_{IJ_1} \times 1/\Omega_{BZ} \int_{BZ} \hat{\tau}(\mathbf{k}') e^{i\mathbf{k}'\cdot(\mathbf{R}_I+\mathbf{R}_{J_2}-\mathbf{R}_j-\mathbf{R}_{I'_1})} d\mathbf{k}' D^{\beta;\gamma'}_{I'j} \right)_{LL'} e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_j)}, \tag{35}
$$

which, allows us to introduce a delta function using

$$
1/N \sum_j e^{i(\mathbf{k}-\mathbf{K}_n)\cdot(\mathbf{R}_I-\mathbf{R}_j)} = \delta(\mathbf{k}-\mathbf{K}_n). \tag{36}
$$

It is crucial in carrying out this step to note that the quantity in Eq. (32) is an ensemble averaged quantity, and as such, it is translationally invariant. We may thus note that the matrix D is therefore independent of the index j (this is equivalent to stating that the NLCPA is set up such that only the *difference* between sites I' and j is important, rather than the choice of origin j) and we may thus choose to relabel this origin as I.

We can now write this term as

$$
\begin{aligned}
& \sum_{\alpha\beta} P(\alpha|I)P(\beta|I) \sum_\gamma \sum_{\gamma'} P(\gamma|\alpha)P(\gamma'|\beta) \\
& \quad \times \sum_{LL'} F^{\alpha\beta}_{LL'} \sum_{I_1,J_1} \left(D^{\dagger\alpha;\gamma}_{I,I_1} \hat{\tau}(\mathbf{K}_n;\mathbf{0}) e^{i\mathbf{K}_n\cdot(\mathbf{R}_{I_1}-\mathbf{R}_{J_1})} D^{\beta;\gamma'}_{J_1,I} \right)_{LL'},
\end{aligned} \tag{37}
$$

where the $\hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}})$ is defined through

$$
\hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}}) = [\hat{t}^{-1} - G(\mathbf{K}_n+\tilde{\mathbf{k}}) - \delta\hat{G}(\mathbf{K}_n)]^{-1}. \tag{38}
$$

Note that this is distinct from the coarse-grained average of the path scattering operator over a reciprocal space tile centered at the point $\mathbf{K}_n$, $\hat{\tau}(\mathbf{K}_n)$. Instead, the quantity $\hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}})$ is the path scattering operator *at the reciprocal space point* $\mathbf{k}=\mathbf{K}_n+\tilde{\mathbf{k}}$, where $\tilde{\mathbf{k}}$ lies within a NLCPA tile centered upon $\mathbf{K}_n$. It is related to the real space path scattering operator $\hat{\tau}^{Ij}$ through

$$
\hat{\tau}^{Ij} = N_c/\Omega_{BZ} \sum_{\mathbf{K}_n} \int_{\Omega_{\mathbf{K}_n}} d\tilde{\mathbf{k}}\, \hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}}) e^{i(\mathbf{K}_n+\tilde{\mathbf{k}})\cdot(\mathbf{R}_I-\mathbf{R}_j)}, \tag{39}
$$

where the integral is taken over the NLCPA tile about $\mathbf{K}_n$.

If we now substitute this in Eq. (31), we obtain the spectral function given by

$$\begin{aligned}A_b(E,\mathbf{K}_n) = -(1/N_c\pi)\mathrm{Im}\Bigg[&\sum_J\left\{\sum_{\alpha\beta}\sum_{\gamma}P(\alpha\beta|IJ)P(\gamma|\alpha\beta)\sum_{LL'}(F^{\alpha\beta}_{LL'}\langle\tau^{IJ}_{LL'}\rangle_{\alpha\beta;\gamma}-\delta_{LL'}\delta_{\alpha\beta}\bar{F}^{\alpha}_{LL'})\right\}e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)}\\&-\sum_J\sum_{\alpha\beta}\sum_{\gamma,\gamma'}P(\alpha|I)P(\beta|J)P(\gamma|\alpha)P(\gamma'|\beta)\sum_{LL'}F^{\alpha\beta}_{LL'}\left(\sum_{J_1,I_2}D^{\dagger\alpha;\gamma}_{IJ_1}\hat{\tau}^{J_1I_2}D^{\beta;\gamma'}_{I_2J}\right)_{LL'}e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)}\\&+\sum_{\alpha\beta}\sum_{\gamma,\gamma'}P(\alpha|I)P(\beta|I)P(\gamma|\alpha)P(\gamma'|\beta)\sum_{LL'}F^{\alpha\beta}_{LL'}\left(\sum_{J_1I_2}D^{\dagger\alpha;\gamma}_{IJ_1}\hat{\tau}(\mathbf{K}_n;\mathbf{0})e^{i\mathbf{K}_n\cdot(\mathbf{R}_{J_1}-\mathbf{R}_{I_2})}D^{\beta;\gamma'}_{I_2I}\right)_{LL'}\Bigg].\end{aligned}\qquad(40)$$

Before presenting the results of calculations with this expression, it is worth discussing some of its features. The expression is similar to that obtained by Faulkner and Stocks for the CPA,[36] and represents the NLCPA generalization of their single-site result. For the special case of $N_c=1$, the spectral function in Eq. (40) reduces to the CPA spectral function, as required.

IV. RESULTS

A. CuZn

In order to examine the validity of our formalism, we present the results of calculations of the spectral function at the NLCPA cluster momenta for the bcc $Cu_{50}Zn_{50}$ solid solution, with lattice constant 2.86 Å. The Cu and Zn potentials in these calculations originate from self-consistent field KKR-CPA calculations,[37,38] the Brillouin zone integrals are carried out using the adaptive quadrature method,[39] and the energy contour has a 1 mRy imaginary part.

CuZn is an archetypal split-band system; that is, the energies of the Cu and Zn d bands are very different. In Fig. 3, the spectral function at the Brillouin zone center for an ordered CuZn solid solution is presented. The split-bands can clearly be observed, with the low energy peaks originating from the Zn sites, and the high energy features corresponding to the Cu sites. For the pure bcc Cu and Zn systems with the same lattice constant we present the zone center spectral functions in Fig. 4. It is worth noting that ordering is energetically preferred for CuZn in the bcc solid solution, and correspondingly, it can be seen that the spectral features in the ordered calculation have been shifted to slightly lower energies with respect to the features present in the pure calculation.

In order to demonstrate the effects of disorder upon the spectral function, we present in Fig. 5 the results of CPA and NLCPA calculations. It is immediately apparent that disordering leads to a broadening and smoothing of the spectral features, which is as expected. In common with the previous work of Rowlands *et al.*, the two-site NLCPA cluster used leads to small nonlocal corrections (of the order of 1 state/atom/Ry in the DOS) and hence there is very little difference in the spectral function compared to the CPA result. The differences that do occur do so within the d bands, again, as expected.

B. Short range order

One of the major motivations for developing the NLCPA is that it allows the effects of short range order (SRO) upon the electronic structure of disordered alloys to be investigated upon an *ab initio* basis. This is in contrast to single-site theories such as the CPA. SRO may be incorporated by suitably weighting the cluster configuration probability distribution. In this work, we use a nearest-neighbor Warren-Cowley parameter α,[40] and define our probabilities to be

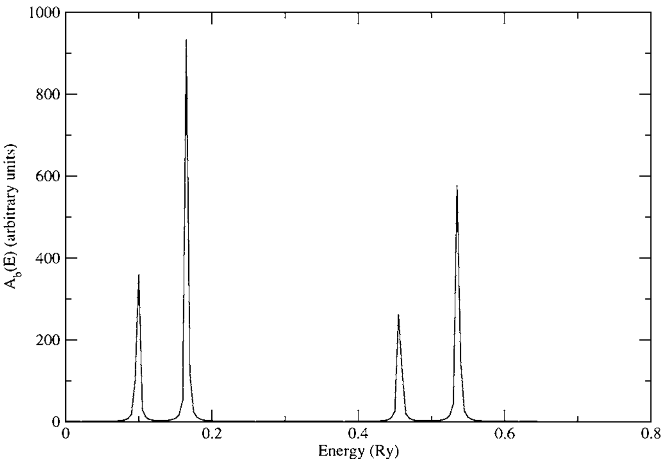

FIG. 3. Spectral function for ordered CuZn solid solution at zone center, $\mathbf{K}_n=(0,0,0)$, $\tilde{\mathbf{k}}=(0,0,0)$.

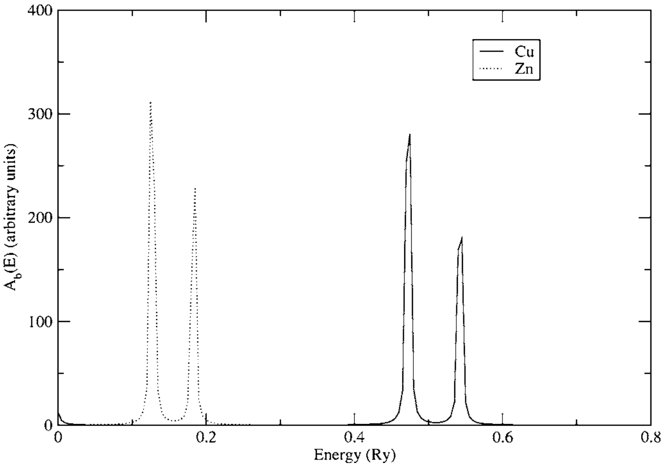

FIG. 4. Spectral function for pure Cu and Zn at zone center, $\mathbf{K}_n=(0,0,0)$, $\tilde{\mathbf{k}}=(0,0,0)$.

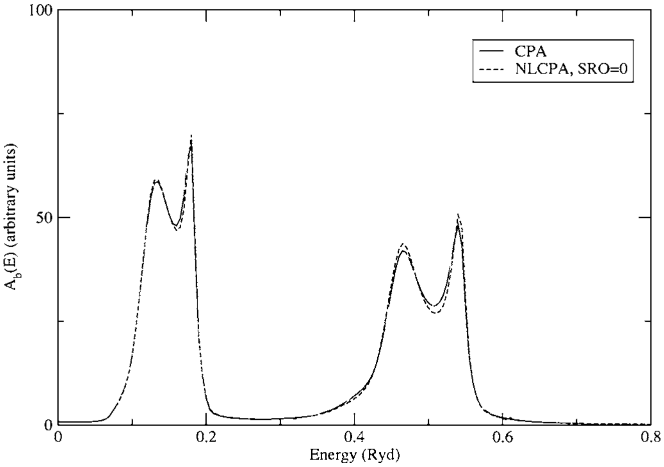

FIG. 5. Spectral function for disordered CuZn solid solution at zone center for both CPA and two-site NLCPA calculations.

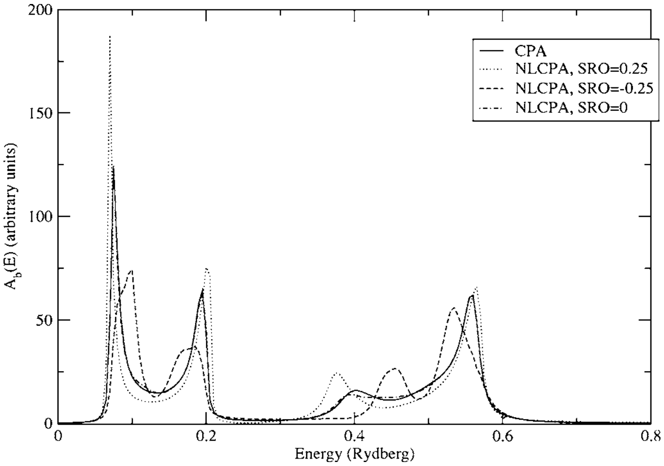

FIG. 7. Spectral function for disordered CuZn solid solution at (0, 0, 1); effects of SRO are also indicated.

$$P(\text{CuCu}) = P(\text{Cu})^2 + \alpha,$$

$$P(\text{ZnZ}n) = P(\text{Zn})^2 + \alpha,$$

$$P(\text{CuZn}) = P(\text{Cu})P(\text{Zn}) - \alpha,$$

$$P(\text{ZnCu}) = P(\text{Zn})P(\text{Cu}) - \alpha. \tag{41}$$

As $P(\text{Cu})=P(\text{Zn})=0.5$ for the binary solid solution in this work, the parameter α may range between values of -0.25 and 0.25, with the former corresponding to ideal ordering, and the latter corresponding to ideal clustering. Complete randomness occurs when $\alpha=0$.

In Fig. 6, the effects of SRO upon the spectral function at the Brillouin zone center $[\mathbf{K}_n=(0,0,0)]$, i.e., the Γ point, are shown. Given that unlike pairs of atoms are not allowed, the results for $\alpha=0.25$ tend towards those of the pure state, with the spectral features becoming more distinct and sharper, as expected. In contrast, the $\alpha=-0.25$ case results in the low energy features originating from the Zn states merging into one peak. This is a quite marked manifestation of the effects of SRO upon the spectral function, and potentially offers the opportunity of experimentalists observing such effects via techniques such as photoemission experiments.[33,34] Note also that the high energy peaks are shifted to lower energies compared to the CPA result, which is consistent with the tendency of CuZn solid solutions to energetically favor ordering. Of course, by choosing $\alpha=-0.25$ we are encouraging the solution to order.

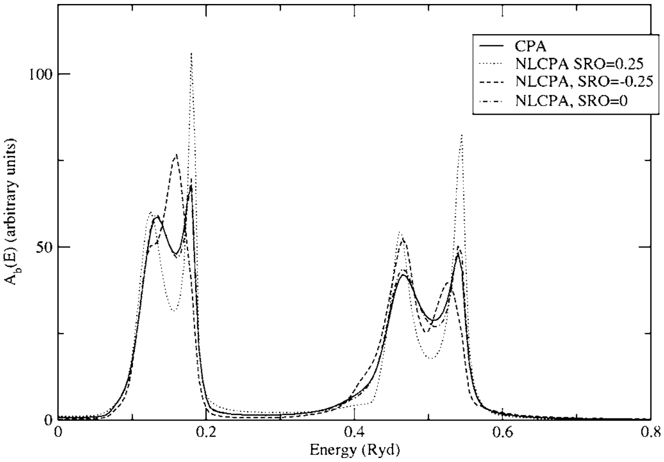

FIG. 6. Spectral function for disordered CuZn solid solution at zone center; effects of SRO.

Figure 7 illustrates the effects of disorder and SRO upon the CuZn spectral function at the point $\mathbf{K}_n=(0,0,1)$, i.e., at the edge of the Brillouin zone (the H point). Again, it can be seen that the result of disorder is to broaden the spectral features present; indeed, the spectral fature in the region of 0.4 Ry is almost entirely smeared out. As at the zone center, the NLCPA result in the absence of SRO is very similar to that of the CPA. Ideal clustering results in the spectral features increasing in definition. It is interesting to note that this also involves a marked increase in the separation of the higher energy Cu peaks, with the spectral feature at 0.4 Ry being shifted down in energy. This shift is accompanied by an increase in spectral weight. Conversely, for the ideal ordering case, the separation of the peaks decreases; again, the effect is most marked for the Cu peaks. This band narrowing can be understood by considering the nature of the split-band regime: physically, this corresponds to electrons propagating more easily between like sites than unlike sites; by ordering the solution, and thus decreasing the overlap between like sites, the bands will accordingly narrow. Note that this is consistent with the increase in band dispersion observed upon clustering.

V. SPECTRAL FUNCTION AT ARBITRARY RECIPROCAL SPACE POINTS

As noted previously, the formalism developed thus far allows a spectral function at the cluster momenta, $\mathbf{K}_n$ ($\tilde{\mathbf{k}}=0$), to be calculated, as all the quantities entering the calculation are well-defined at these reciprocal space points. This lends itself naturally then to "energy scans," whereby one calculates the spectral function for a range of energies at these fixed k points. In practice, however, one often wishes to calculate the spectral function along given lines in reciprocal space for a particular energy. Such calculations are particularly useful, for example, in examining the Fermi surface topology of a system.[32]

In order to understand how to obtain a spectral function at an arbitrary point $\mathbf{k}$, we need to consider how to deal with the three terms in Eq. (40). The first two terms are straightforward to deal with: they are cluster diagonal quantities, and therefore, within the NLCPA, remain constant for all values of $\mathbf{k}$ within a given tile centered on $\mathbf{K}_n$. They are specified therefore at these cluster momenta $\mathbf{K}_n$ and accordingly remain unaltered. The third term has the form of a product of three Fourier transforms, i.e., $\int A^{\dagger}(\mathbf{K}_n,\mathbf{r}_I)\hat{\tau}(\mathbf{K}_n;\mathbf{0})A(\mathbf{K}_n,\mathbf{r}_I)d\mathbf{r}_I$, where we have defined the matrix $\underline{A}$ as

$$A_{IJ}^{\alpha;\gamma}(\mathbf{K}_n,\mathbf{r}_I) = \sum_{J}\sum_{\alpha}\sum_{\gamma} P(\alpha|I)P(\gamma|\alpha)Z^{\alpha}(E,\mathbf{r}_I)D_{IJ}^{\alpha;\gamma}e^{i\mathbf{K}_n\cdot\mathbf{R}_J} \tag{42}$$

of which the matrix $\underline{A}$ and its transpose are cluster diagonal. Similarly, these quantities are specified at the cluster momenta in reciprocal space. Conversely, $\hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}})$ is not cluster diagonal; and can vary from point to point in reciprocal space, the reciprocal space dependence arises from the free space structure constants [see Eq. (38)]. Following these arguments, the spectral function at an arbitrary k point is given by the expression

$$\begin{aligned} A_b(E,\mathbf{k}) = -(1/N_c\pi)\mathrm{Im}\Bigg[& \sum_{J}\Bigg\{\sum_{\alpha\beta}\sum_{\gamma} P(\alpha\beta|IJ)P(\gamma|\alpha\beta)\sum_{LL'}(F_{LL'}^{\alpha\beta}\langle\tau_{LL'}^{IJ}\rangle_{\alpha\beta;\gamma} - \delta_{LL'}\delta_{\alpha\beta}\bar{F}_{LL'}^{\alpha})\Bigg\}e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)} \\ & -\sum_{J}\sum_{\alpha\beta}\sum_{\gamma,\gamma'} P(\alpha|I)P(\beta|J)P(\gamma|\alpha)P(\gamma'|\beta)\sum_{LL'}F_{LL'}^{\alpha\beta}\Bigg(\sum_{J_1I_2}D_{IJ_1}^{\dagger\alpha;\gamma}\hat{\tau}^{J_1I_2}D_{I_2J}^{\beta;\gamma'}\Bigg)_{LL'}e^{-i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_J)} \\ & +\sum_{\alpha\beta}\sum_{\gamma,\gamma'} P(\alpha|I)P(\beta|I)P(\gamma|\alpha)P(\gamma'|\beta)\sum_{LL'}F_{LL'}^{\alpha\beta}\Bigg(\sum_{J_1I_2}D_{IJ_1}^{\dagger\alpha;\gamma}\hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}})e^{i\mathbf{K}_n\cdot(\mathbf{R}_{J_1}-\mathbf{R}_{I_2})}D_{I_2I}^{\beta;\gamma'}\Bigg)_{LL'}\Bigg]. \end{aligned} \tag{43}$$

This yields a fully causal spectral function at any reciprocal space point, and represents the natural NLCPA extension of the KKR-CPA spectral function. To illustrate this, recall that in the CPA, the first two terms provide a constant background across the Brillouin zone, the first of which is simply the density of states; the remaining $\mathbf{k}$-dependent term is then responsible for the fluctuations in the electronic structure in reciprocal space about this mean background, and integrating over the Brillouin zone yields the density of states. Similarly, in Eq. (43), the first two terms represent the average of the electronic states over a NLCPA reciprocal space tile; the k dependent third term then fulfills a role similar to that in the CPA case, and describes the detailed form of the electronic structure within a reciprocal space tile. Integrating over a tile, we obtain the coarse-grained average spectral function presented earlier in Eq. (22), i.e., the density of states of a particular tile. We can see therefore, that the expression in Eq. (43) is indeed the correct generalization of the single-site result of Faulkner and Stocks[36] for the NLCPA spectral function at an arbitrary k point. We should note however, that the $\underline{\delta\hat{G}}(\mathbf{K}_n)$ term in $\hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}})$ is constant over a given reciprocal space tile; this may lead to discontinuities at tile boundaries, which may be removed by a suitable smoothing scheme.

A. Application to CuNi solid solution

To illustrate calculation of the spectral function along specific lines in reciprocal space, in this section we examine the fcc $\mathrm{Cu_{77}Ni_{23}}$ solid solution with a 6.76 Å lattice constant. As in the CuZn calculations described previously, self-consistent KKR-CPA potentials are used. A four-site cluster is used, and short-range order is introduced into the calculation analogously to the CuZn case study.

The following motivates our choice of CuNi: it has a different lattice structure to CuZn, being fcc, and therefore allows us to illustrate the efficacy of the NLCPA when applied to systems with larger clusters; as a classic example of a binary alloy a wealth of theoretical and experimental work[2,33,34,41–44] exists discussing its electronic structure with which we can compare results; and lastly, although a split-band system,[43] the electronic structure is sufficiently different from that of CuZn to provide a further test of the formalism presented.

We begin by examining the density of states, which is illustrated in Fig. 8. The $\mathrm{Cu_{77}Ni_{23}}$ solid solution is widely known to be in the split-band regime,[43] although in contrast to the CuZn system, the Cu and Ni features are less widely separated in energy. Indeed, Fig. 8 shows the resulting Ni impurity bands that occur at an energy of just less than 0.6 Ry, which in the CPA case, are visible as a shoulder. The mass of spectral features observed in the energy range of approximately 0.2–0.5 Ry arise from the Cu d bands. Note that the NLCPA four-site cluster calculation reproduces, in the main, the CPA density of states (DOS) to a high degree of agreement. It is interesting however, to note that the nonlocal corrections to the electronic propagation result in a more distinct Ni impurity band occurring, even in the absence of SRO. This is in agreement with the experimental results of Seib and Spicer,[34] and suggests that incorporation of nonlo-

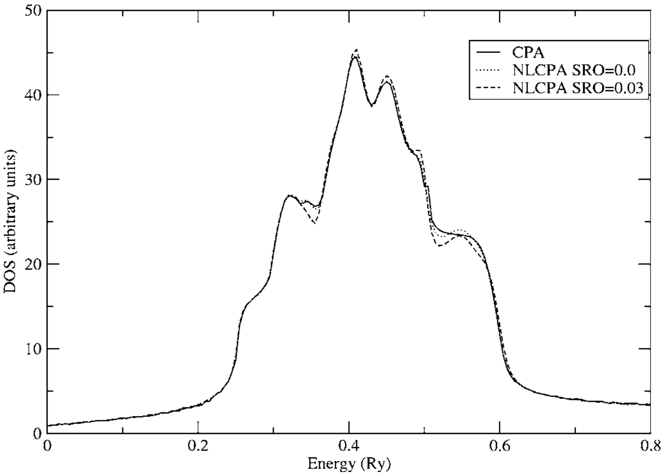

FIG. 8. CuNi solid solution density of states

cal effects is essential to correctly describe this spectral feature.

If we switch on the effects of SRO by increasing the value of the SRO parameter to 0.03, then this models the experimentally known tendency of CuNi systems to cluster.[34] This clustering is accompanied by a transfer of spectral weight from the low energy Cu feature at around 0.35 Ry and the Ni impurity band to the Cu *d*-band peaks. Indeed, we note that a small feature is observed at around 0.3 Ry. The transfer of spectral weight, and in particular, the reduction in the DOS at the Ni impurity bands, may be understood if one considers that upon clustering, the electronic structure will approach that of the pure Cu and Ni systems.

Having examined the DOS, we now present an example of the spectral function along the direction (0,0,0) to (0,0.5,1) (the *W* point) at 0.353 Ry in Fig. 9. We choose this energy because the DOS plot indicates a large alteration in spectral weight occurring at this energy upon increase of SRO. The CPA and NLCPA (no SRO) results are similar, although visible discrepancies indicate the effects of nonlocal scattering corrections.

The presence of SRO can be seen to result in the spectral features losing weight, accompanied by an increase in the separation of the peaks. This reflects an increase in band dispersion, and is to be expected, given that the clustering regime results in an atom being preferentially surrounded by like neighbors. The increased overlap between neighboring sites accompanying this then leads to band broadening as observed.

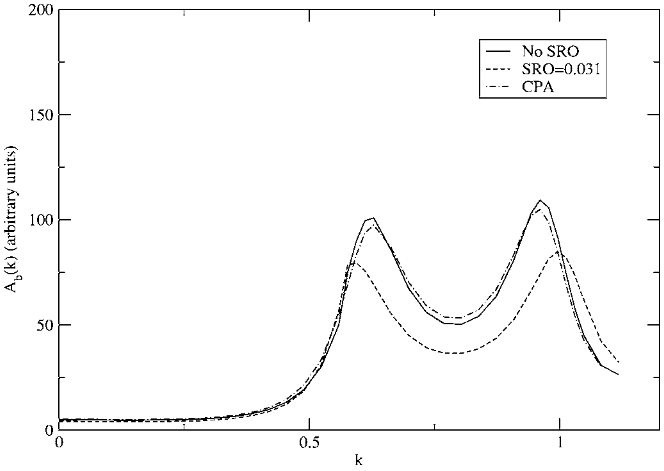

FIG. 9. Spectral function for disordered CuNi solid solution along the direction (0,0,0) to (0,0.5,1.0) at 0.353 Ry.

VI. CONCLUSIONS

In this paper we have demonstrated how the KKR-NLCPA leads naturally to a coarse-grained average of the spectral function over a reciprocal space tile, and have presented a formalism that allows the calculation of a Bloch spectral function at any point in reciprocal space within the KKR-NLCPA framework. This spectral function is fully causal, and allows the effects of short-range order upon the electronic structure of random alloys to be investigated. We have illustrated the efficacy of the formalism by examining the electronic structure of the bcc $Cu_{50}Zn_{50}$ and the fcc $Cu_{77}Ni_{23}$ solid solutions.

The spectral function offers information on the electronic structure in addition to that contained in the density of states, whilst a knowledge of the reciprocal space distribution of the electronic states allows contact to be made with experimental measurements through such techniques as positron annihilation and photoemission; this potentially allows the use of such techniques as probes of the level of SRO present in sample materials, which has important technological implications.

It is hoped that the work presented here can form the basis of an investigation into the effects of SRO upon the Fermi surface of transition metal alloys. Further, it is our intention to extend the NLCPA formalism to allow investigation of the role of SRO in itinerant metallic magnets.

ACKNOWLEDGMENTS

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APPENDIX: RESTRICTED AVERAGES IN NLCPA

In calculating the spectral function, we need to calculate restricted averages of the form $\langle \hat{\tau}^{IJ'} \rangle_{\alpha;\gamma:\alpha';\gamma'}$, where sites I and J' lies in different clusters. In an earlier section, it was asserted that these averages may be given by

$$\langle \tau^{IJ'}_{LL'} \rangle_{\alpha;\gamma:\alpha';\gamma'} = \sum_{J,I'} D^{\dagger\alpha;\gamma}_{IJ} \hat{\tau}^{JI'} D^{\alpha';\gamma'}_{I'J'} . \tag{A1}$$

In order to justify this, we begin by considering a general configuration of scatterers, for which we can write that

$$\sum_{k} [t_k^{-1} \delta_{ik} - G(\mathbf{R}_{ik})] \tau^{kj} = \delta_{ij}, \tag{A2}$$

where $G(\mathbf{R}_{ik})$ is the free electron Green's function. Expanding about the NLCPA medium yields

$$\sum_{k}[(t_k^{-1}-\hat{t}^{-1})\delta_{ik}+\delta\hat{G}(\mathbf{R}_{ik})+\hat{t}^{-1}-\delta\hat{G}(\mathbf{R}_{ik})-G(\mathbf{R}_{ik})]\tau^{kj}=\delta_{ij} \tag{A3}$$

or,

$$\sum_{k}[(\hat{\tau}^{-1})^{ik}+\delta t_k^{-1}\delta_{ik}+\delta\hat{G}(\mathbf{R}_{ik})]\tau^{kj}=\delta_{ij}, \tag{A4}$$

where

$$\delta t_k^{-1}=t_k^{-1}-\hat{t}^{-1}. \tag{A5}$$

After some simple algebra, this may be written as follows:

$$\tau^{ij}=\hat{\tau}^{ij}-\sum_{k,l}\hat{\tau}^{ik}[\delta t_k^{-1}\delta_{kl}+\delta\hat{G}(\mathbf{R}_{kl})]\tau^{lj}. \tag{A6}$$

In order to find the average of τ^{ij}, we now make an approximation: in the above double summation, the index k is taken to be summed over a set of NLCPA cluster sites about site i, whilst the index l is similarly summed, but over a separate set of cluster sites about j. That is, we consider fluctuations about the NLCPA medium over a cluster extent, and treat the clusters independently. This is the NLCPA cluster generalization of the single-site result obtained by Faulkner and Stocks in the context of the CPA.[36] If now we consider these two clusters, then we can write, upon averaging, that

$$\begin{aligned}\langle\tau^{IJ'}\rangle_{\alpha,\gamma;\alpha',\gamma'} \approx\ & \hat{\tau}^{IJ'}-\sum_{JK}\hat{\tau}^{IJ}(\delta t_J^{-1}(\alpha,\gamma)\delta_{JK}+\delta\hat{G}(\mathbf{R}_{JK}))\\ & \times\langle\tau^{KJ'}\rangle_{\alpha,\gamma;\alpha',\gamma'}-\sum_{K'L'}\hat{\tau}^{IK'}(\delta t_{K'}^{-1}(\alpha',\gamma')\delta_{K'L'}\\ & +\delta\hat{G}(\mathbf{R}_{K'L'}))\langle\tau^{L'J'}\rangle_{\alpha',\gamma'},\end{aligned} \tag{A7}$$

and

$$\begin{aligned}\langle\tau^{L'J'}\rangle_{\alpha',\gamma'} \approx\ & \hat{\tau}^{L'J'}-\sum_{M',N'}\hat{\tau}^{L'M'}(\delta t_{M'}^{-1}(\alpha',\gamma')\delta_{M'N'}\\ & +\delta\hat{G}(\mathbf{R}_{M'N'}))\langle\tau^{N'J'}\rangle_{\alpha',\gamma'}\end{aligned} \tag{A8}$$

where I,J, etc., lie in one cluster and primed indices denote sites in another cluster.

Recalling the definition of the matrix $\underline{M}$ in Eq. (30), and recalling that the matrix $\underline{D}$ is the inverse of $\underline{M}$, this implies

$$\begin{aligned}\langle\tau^{IJ'}\rangle_{\alpha,\gamma;\alpha',\gamma'} =\ & \sum_{K}D_{IK}^{\dagger\alpha;\gamma}\hat{\tau}^{KJ'}-\sum_{K}D_{IK}^{\dagger\alpha;\gamma}\sum_{LM}\hat{\tau}^{KL}(\delta t_L^{-1}(\alpha,\gamma)\delta_{LM}\\ & +\delta\hat{G}(\mathbf{R}_{LM}))\sum_{N'}\hat{\tau}^{MN'}D_{N'J'}^{\alpha';\gamma'}.\end{aligned} \tag{A9}$$

Using the definition of the matrix $\underline{M}$, some simple manipulations yield the desired result

$$\langle\tau^{IJ'}\rangle_{\alpha,\gamma;\alpha',\gamma'}=\sum_{JI'}D_{IJ}^{\dagger\alpha;\gamma}\hat{\tau}^{JI'}D_{I'J'}^{\alpha';\gamma'}. \tag{A10}$$

We note further that the matrix $\underline{D}$ satisfies the sum rule

$$\sum_{\gamma}P(\gamma)D_{IJ}^{\alpha;\gamma}=\delta_{IJ} \tag{A11}$$

which is an alternative expression of the NLCPA condition in Eq. (14). Using this, we can write

$$\sum_{\gamma,\gamma'}P(\gamma)P(\gamma')\sum_{JI'}D_{IJ}^{\dagger\alpha;\gamma}\hat{\tau}^{JI'}D_{I'J'}^{\alpha';\gamma'}=\hat{\tau}^{IJ'} \tag{A12}$$

which is an expression for the effective medium path scattering operator connecting sites in different NLCPA clusters.

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