PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 48, NUMBER 3 15 JULY 1993-I

Disordered alloys with short-range order: A Korringa-Kohn-Rostoker formulation within the cluster coherent-potential approximation

S. S. A. Razee and R. Prasad
Department of Physics, Indian Institute of Technology, Kanpur 208016, India

(Received 23 October 1992; revised manuscript received 17 February 1993)

We present a generalization of the Korringa-Kohn-Rostoker cluster coherent-potential approximation for systems with short-range order (SRO). For this purpose we have used the generalized augmented-space formalism of Gray and Kaplan, in which one can deal with independent (corresponding to purely random systems) as well as dependent (corresponding to systems with SRO) random variables. The expression for the configuration-averaged Green's function in this case is essentially an expansion about the Green's function for a purely random system, and contains an infinite number of terms. For simplicity, we truncate the series after the second-order correction term. Using this approximation, we have calculated the density of states (DOS) for a one-dimensional muffin-tin alloy with Markovian-type SRO and find that the introduction of SRO can produce large changes in the DOS. We also find that the approximation yields non-negative DOS at all energies for a reasonably wide range of SRO parameter.

I. INTRODUCTION

Most disordered alloys in nature exhibit some degree of short-range order (SRO), some common and well-known examples being CuAu,[1,2] CuAl,[3] AuPd,[4] NiPt,[5] CuPt,[6,7] CuPd,[7,8] AlZn and AlAg,[9] etc. By SRO we mean the tendency of atoms of a given kind to surround atoms of the same kind (clustering) or of a different kind (ordering). In the presence of SRO, the probability of a particular kind of atom occupying a given site on the lattice can no longer be determined by the concentrations of the constituents alone, but the surrounding environment of the site also plays a role. Therefore, the theories which are developed for purely random alloys cannot be applied to systems which exhibit SRO. In this paper we will focus only on the electronic structure of such alloys, which plays a central role in the calculation and understanding of various physical properties of the alloys. The application of existing theories of random alloys to the systems with SRO can yield unsatisfactory results. An example being the CuPd system in which the Korringa-Kohn-Rostoker coherent-potential approximation[10,11] (KKR-CPA) gives different results from experiment.[12]

There have been several attempts at developing a theory of electronic properties of disordered alloys with SRO.[13-17] Gonis and Freeman[15] have used the embedded cluster method,[18] which is a non-self-consistent approach. The work of Gray and Kaplan[13,14] is a self-consistent approach. However, this approach is within the tight-binding framework, and therefore, not parameter-free. In order to perform a first-principles parameter-free calculation of the electronic properties of such alloys, one has to develop a theory either in the KKR Green's-function formulation[10,11] or within the linear-muffin-tin-orbital method.[19] Banhart *et al.*[20] have used the embedded cluster method[18] within the KKR-CPA framework to study the effects of SRO in CuPt, but this method is not cluster self-consistent.

It is clear that the problem of SRO cannot be treated within the single-site approximations and a cluster or multisite theory should be used. Recently,[21-24] we have developed the KKR cluster coherent-potential approximation (KKR-CCPA) for purely random alloys by combining the augmented space formalism[25] (ASF) and the conventional KKR Green's-function formulation.[10,11] This formalism is a first-principles parameter-free theory within the local density-functional theory[26] and it takes into account the correlated scattering from more than one site. Our aim in this paper is to extend this theory so as to include the effects of SRO. The ASF of Mookerjee,[25] which was used to develop the KKR-CCPA formulation, has the restriction that the probability of a particular kind of atom occupying a given site is completely independent of the surrounding environment. This assumption is not valid for systems with SRO. Disordered systems with SRO can only be described in terms of dependent random variables. Gray and Kaplan[14] have shown that ASF can be generalized so as to deal with dependent random variables as well. This generalized ASF has already been applied to disordered alloys in the tight-binding framework. In the present work, we have used this technique in the KKR framework.

0163-1829/93/48(3)/1349(7)/$06.00

Using generalized ASF we have derived an expression for the configuration-averaged Green's function for systems with SRO. We find that this expression is essentially an expansion of the configuration-averaged Green's function in the presence of SRO about that for a purely random system. This Green's function is herglotz and guarantees a non-negative density of states (DOS) at all energies (as shown in the Appendix). However, for numerical computations, we have truncated the series after the second-order correction term in the expansion. It turns out that the first-order correction term vanishes identically, and within the CCPA with a two-atom cluster, the second-order term gives us only one nonvanishing term. Thus, our formalism allows us to calculate the properties of a system with SRO in terms of the random average of the Green's function and without any substantial amount of additional computational effort.

We have used this approximated averaged Green's function to calculate the DOS for a one-dimensional muffin-tin alloy with Markovian-type SRO.[14] We have calculated the DOS for the alloy with different SRO parameters. We observe large changes in the DOS due to introduction of SRO. Also, we find that the DOS remains non-negative throughout the whole energy region for a fairly wide range of the SRO parameter. However, in the strong SRO regime the DOS becomes negative in certain energy regions. This unphysical behavior is due to the approximation in which the higher-order correction terms in the expansion of the configuration-averaged Green's function are neglected. It thus turns out that the approximation which we have used fails only in the strong SRO regime. The breakdown of the approximation in this regime may be due to the fact that the higher-order terms in the expansion of the Green's function become important in the strong SRO regime. We have compared our results with those obtained by the embedded cluster method of Gonis and Freeman.[15] In this method, a two-atom cluster is embedded in the KKR-CPA medium, with the probabilities of different pairs depending upon the choice of the SRO parameter. We find that there is a general agreement between the two results.

The outline of the paper is as follows. In Sec. II we present our formulation. We have derived the expression for the configuration-averaged Green's function using the generalized augmented space theorem and we give an expression for the configuration-averaged Green's function within the CCPA, which is used in the computation. In Sec. III, we describe the Markovian-type SRO and in Sec. IV, we present the results of our calculation. Finally, in Sec. V we give our conclusions.

II. FORMULATION

A particular configuration of a disordered alloy can be described in terms of a set of occupation variables $\{n_i\}$ in a particular sequence, and a certain probability density $\mathcal{P}(\{n_i\})$ are associated with each of these configurations. The simplest case that represents a disordered alloy is one in which $\{n_i\}$ are independent random variables. This represents a purely random alloy. In this case, it is possible to decompose $\mathcal{P}(\{n_i\})$ into a product of individual probability densities of all the sites, i.e.,

$$\mathcal{P}_{\text{random}}(\{n_i\})=\prod_i p_i(n_i) \ . \tag{1}$$

However, when $\{n_i\}$ are not statistically independent, as is the case with systems with SRO, such a decomposition is not possible. Nevertheless, it is possible to decompose $\mathcal{P}_{\text{SRO}}(\{n_i\})$, the probability distribution function in the presence of SRO, into two parts such that the SRO part is separated. Gray and Kaplan[14] have shown from a "measure theoretical" argument that one can write

$$\begin{aligned}\mathcal{P}_{\text{SRO}}(\{n_i\})&=\phi(\{n_i\})\mathcal{P}_{\text{random}}(\{n_i\})\\&=\phi(\{n_i\})\prod_i p_i(n_i) \ ,\end{aligned} \tag{2}$$

where $\phi(\{n_i\})$ is the Radon-Nikodym derivative[27] of $\mathcal{P}_{\text{SRO}}(\{n_i\})$ with respect to $\mathcal{P}_{\text{random}}(\{n_i\})$.

The advantage of Eq. (2) is that it allows one to calculate configuration-averaged properties of a system with SRO in terms of averages which are computed with respect to independent random variables. The price one pays for this simplification is the introduction of an unknown function $\phi(\{n_i\})$. However, we will see later that it can be eliminated from the final expression if the SRO parameters are known.

Now, the configuration-averaged Green's function in the presence of SRO can be written as the integral

$$\langle G\rangle_{\text{SRO}}=\int G(\{n_i\})\mathcal{P}_{\text{SRO}}(\{n_i\})\prod_i dn_i \ . \tag{3}$$

With the help of Eq. (2), we can rewrite Eq. (3) as

$$\langle G\rangle_{\text{SRO}}=\int G(\{n_i\})\phi(\{n_i\})\prod_i p_i(n_i)dn_i \ . \tag{4}$$

Now we are in a position to apply the augmented space theorem[25] to Eq. (4), which gives us

$$\langle G\rangle_{\text{SRO}}=\langle F|\tilde{G}(\{M^i\})\tilde{\phi}(\{M^i\})|F\rangle \ , \tag{5}$$

where $\tilde{G}(\{M^i\})$ and $\tilde{\phi}(\{M^i\})$ are, respectively, obtained by replacing $\{n_i\}$ in $G(\{n_i\})$ and $\phi(\{n_i\})$ by $\{M^i\}$. The state $|F\rangle$ is the "ground state" and M^i is an operator in the configuration space.[28]

In order to use Eq. (5), we need to know $\tilde{\phi}(\{M^i\})|F\rangle$. We note that $\tilde{\phi}(\{M^i\})$ is a function of $\{M^i\}$ only and, therefore, is an operator functional in the configuration space alone (i.e., it is independent of the real Hilbert space). Thus, we can expand $\tilde{\phi}(\{M^i\})|F\rangle$ in terms of the complete set of basis vectors in the configuration space, i.e.,

$$\tilde{\phi}(\{M^i\})|F\rangle=\sum_\sigma a_\sigma|F_\sigma\rangle \ , \tag{6}$$

where

$$a_\sigma=\langle F_\sigma|\tilde{\phi}(\{M^i\})|F\rangle \ . \tag{7}$$

Substituting Eq. (6) in Eq. (5) we get

$$\langle G\rangle_{\text{SRO}}=\sum_\sigma a_\sigma\langle F|\tilde{G}(\{M^i\})|F_\sigma\rangle \ . \tag{8}$$

The coefficients a_σ can be easily determined from known joint distribution functions, and Gray and Kaplan[14] have found that these coefficients are as

$$
\begin{aligned}
&a_{\varnothing}=1\ ,\\
&a_i=0 \text{ for all } i\ ,\\
&a_{ij}=[P^{ij}_{AA}-x^2]/(xy)\ ,\\
&a_{ijk}=[P^{ijk}_{AAA}-x(P^{ij}_{AA}+P^{jk}_{AA}+P^{ki}_{AA})-2x^3]/(xy)^{3/2}\ ,
\end{aligned}
\tag{9}
$$

and so on, where $P^{ij\cdots l}_{AA\cdots A}$ represents the probability of having A-type atoms on $(i,j,\ldots,l)$ sites and $\varnothing$ denotes the null set.

The right-hand side of Eq. (8) is an infinite series. The first term in the series, which is $\langle F|\widetilde{G}(\{M^i\})|F\rangle$, is the configuration-averaged Green's function for a purely random system. Therefore, Eq. (8) can be regarded as a perturbation expansion of the configuration-averaged Green's function in the presence of SRO, about its value for a purely random system. Thus, Eq. (8) allows us to calculate the configuration-averaged Green's function in the presence of SRO, in terms of its random average. In the Appendix, we show that Eq. (5) and equivalently, Eq. (8), would yield non-negative DOS at all energies.

The site-diagonal (SD) form of the KKR-Green's function for a particular configuration of the alloy is given by[21]

$$G_{\mathrm{SD}}(\mathbf{r},\mathbf{r}')=\mathrm{Tr}[T^{ii}U^i]-\sum_L Z^i_L(\mathbf{r}_i)J^i_L(\mathbf{r}'_i)\ , \tag{10}$$

where Tr stands for trace over the angular momentum index L, T^{ii}_{LL} is the path-operator matrix, and

$$U^i_{LL'}=Z^i_L(\mathbf{r}_i)Z^i_{L'}(\mathbf{r}'_i)\ . \tag{11}$$

In Eqs. (10) and (11), $Z^i_L(\mathbf{r}_i)$ and $J^i_L(\mathbf{r}_i)$ are, respectively, the regular and irregular solutions of the Schrödinger equation for a single muffin-tin potential centered on the ith site. In terms of random variables $\{n_i\}$, which take the value 1 when the ith site is occupied by an A-type atom and 0 when occupied by a B-type atom, Eq. (10) can be rewritten as

$$G_{\mathrm{SD}}(\mathbf{r},\mathbf{r}')=\mathrm{Tr}[T^{ii}(U^B+\delta U n_i)]-\sum_L Z^i_L(\mathbf{r}_i)J^i_L(\mathbf{r}'_i)\ , \tag{12}$$

where

$$\delta U=U^A-U^B\ . \tag{13}$$

Using Eq. (8), we can write the configuration-averaged Green's function as

$$\langle G_{\mathrm{SD}}\rangle_{\mathrm{SRO}}=\langle G_{\mathrm{SD}}\rangle+\mathrm{Tr}\left[\sum_{\sigma\neq\varnothing}a_\sigma\{\langle 0;F|[\widetilde{A}(\{M^i\})]^{-1}|0;F_\sigma\rangle U^B+\langle 0;F|[\widetilde{A}(\{M^i\})]^{-1}M^0|0;F_\sigma\rangle\delta U\}\right]\ , \tag{14}$$

where $\langle G_{\mathrm{SD}}\rangle$ is the average Green's function for a purely random system and

$$
\begin{aligned}
\widetilde{A}(\{M^i\})=&\left[C^B\sum_i|i\rangle\langle i|-\sum_{ij(i\neq j)}B^{ij}|i\rangle\langle j|\right]\\
&\otimes\sum_\sigma|F_\sigma\rangle\langle F_\sigma|+\delta C\sum_i|i\rangle\langle i|\otimes M^i\ .
\end{aligned}
\tag{15}
$$

Here, B^{ij} is the real-space version of the KKR structure constants[10,11] and

$$\delta C=C^A-C^B\ , \tag{16}$$

where C^α ($\alpha=A$ or B) is the inverse of the single muffin-tin scattering matrix.

Since Eq. (14) involves an infinite sum, it cannot be used for numerical computations. To make it computationally tractable, we will have to adopt some approximation. We use the approximation which was earlier suggested by Gray and Kaplan.[14] In this approximation, the infinite series in Eq. (14) is truncated after only the second-order correction. Note that this approximation is in addition to CCPA. In this case, only a_{ij} is nonzero [because, according to Eq. (9), all a_i's are zero]. When we invoke the KKR-CCPA to the present case, the number of nonvanishing terms is further reduced. For a two-atom cluster consisting of sites 0 and 1, the only nonzero term in the expansion corresponds to the coefficient a_{01}. This essentially means that we keep only the first correction term of Eq. (8). With this approximation, Eq. (14) becomes

$$
\begin{aligned}
\langle G_{\mathrm{SD}}\rangle_{\mathrm{SRO}}=&\langle G_{\mathrm{SD}}\rangle\\
&+\frac{1}{xy}[P^{01}_{AA}-x^2]\\
&\times\mathrm{Tr}[\langle 0;F|\widetilde{A}^{-1}|0;F_{01}\rangle U^B\\
&+\langle 0;F|\widetilde{A}^{-1}M^0|0;F_{01}\rangle\delta U]\ .
\end{aligned}
\tag{17}
$$

Using the relation in the augmented space[29]

$$M^0|F_{01}\rangle=y|F_{01}\rangle+(xy)^{1/2}|F_1\rangle\ , \tag{18}$$

we rewrite Eq. (17) as

$$
\begin{aligned}
\langle G_{\mathrm{SD}}\rangle_{\mathrm{SRO}}=&\langle G_{\mathrm{SD}}\rangle\\
&+\frac{1}{xy}[P^{01}_{AA}-x^2]\\
&\times\mathrm{Tr}[\langle 0;F|\widetilde{A}^{-1}|0;F_{01}\rangle\widetilde{U}\\
&+\langle 0;F|\widetilde{A}^{-1}|0;F_1\rangle\delta U]\ ,
\end{aligned}
\tag{19}
$$

where

$$\tilde{U}=yU^{A}+xU^{B} . \tag{20}$$

The matrix elements of $\tilde{A}^{-1}$ appearing in Eq. (19) can be calculated easily within the KKR-CCPA (for a two-atom cluster). These are given by[24]

$$\begin{aligned}\langle 0;F|\tilde{A}^{-1}|0;F_{01}\rangle=(xy)^{1/2}\delta C &\times[(C_{\text{eff}}-\xi^{00})Q^{00}\\ &-(V^{01}+b^{01})Q^{01}]\end{aligned} \tag{21}$$

and

$$\begin{aligned}\langle 0;F|\tilde{A}^{-1}|0;F_{1}\rangle=xy(C_{\text{eff}}-\xi^{00})\delta C R_{4}^{-1}\delta C &\times(V^{01}R_{1}^{-1}V^{10}-R_{5}^{-1})^{-1}\\ &-(xy)^{1/2}(V^{01}+b^{01})\delta C b^{10} ,\end{aligned} \tag{22}$$

where C_{eff}, b^{01}, ξ^{00}, Q^{00}, Q^{01}, V^{ij}, and R_i are given by Eqs. (A10)–(A15) of Ref. 21. The random average of the site-diagonal Green's function $\langle G_{\text{SD}}\rangle$ is given by[23]

$$\langle G_{\text{SD}}\rangle=\text{Tr}\left[T_{\text{eff}}^{00}[\bar{U}+(C_{\text{eff}}-\bar{C})(\delta C)^{-1}\delta U]-\sum_{j\in\mathbb{C}}T_{\text{eff}}^{ij}b^{ji}(\delta C)^{-1}\delta U\right]-\sum_{L}[xZ_{L}^{A}(\mathbf{r})J_{L}^{A}(\mathbf{r}')+yZ_{L}^{B}(\mathbf{r})J_{L}^{B}(\mathbf{r}')] , \tag{23}$$

where

$$\bar{U}=xU^{A}+yU^{B} , \tag{24}$$

and

$$\bar{C}=xC^{A}+yC^{B} . \tag{25}$$

The only unknown quantity in Eq. (19) is P_{AA}^{01}, which depends upon the SRO parameter and will be defined in the next section.

III. MARKOV CHAIN

This is the simplest possible system for which the SRO can be easily defined. In a Markov chain, the occupation probability of a particular site is assumed to depend only on the kind of atoms occupying its first nearest-neighbor sites. Therefore, in a Markov chain, the SRO is restricted to nearest-neighbor pairs only. The Warren-Cowley SRO parameter[30–33] α for a nearest-neighbor pair is defined as

$$\alpha=1-\frac{p(A,B)}{y} , \tag{26}$$

where $p(A,B)$ is the probability of finding a B-type atom as a nearest neighbor of an A-type atom. The nearest-neighbor pair probability distribution function can be written in terms of α in the following way:

$$\begin{aligned}p(n_i=1,n_j)=&(x+\alpha y)\delta(n_j-1)\\ &+(1-\alpha)y\delta(n_j)\end{aligned} \tag{27}$$

and

$$\begin{aligned}p(n_i=0,n_j)=&(1-\alpha)x\delta(n_j-1)\\ &+(y+\alpha x)\delta(n_j) .\end{aligned} \tag{28}$$

It is easily seen that the condition $\alpha=0$ represents a purely random system, $\alpha<0$ represents a system in which AB- and BA-type orderings are favored, and $\alpha>0$ represents a system in which AA- and BB-type clustering would be dominant. The maximum value of α is that for which $x+\alpha y=y+\alpha x=1$, which gives us

$$\alpha_{\max}=1 , \tag{29}$$

and this corresponds to a system in which A- and B-type atoms are completely segregated. The minimum value of α is that for which $\min(x+\alpha y,y+\alpha x)=0$ (otherwise, one of the probabilities will become negative), which gives us

$$\alpha_{\min}=-\min\left[\frac{x}{y},\frac{y}{x}\right] . \tag{30}$$

In this case, AA- and BB-type pairs will not exist and for a 50-50 alloy, this will correspond to a situation, when the alloy is not random at all, but forms a superlattice of A and B constituents. The different pair probabilities can now be written as

$$\begin{aligned}P_{AA}^{01}&=xp(n_0=1,n_1=1)=x^2+\alpha xy ,\\ P_{AB}^{01}&=xp(n_0=1,n_1=0)=(1-\alpha)xy ,\\ P_{BA}^{01}&=xp(n_0=0,n_1=1)=(1-\alpha)xy ,\\ P_{BB}^{01}&=xp(n_0=1,n_1=0)=y^2+\alpha xy .\end{aligned} \tag{31}$$

We will use this form of P_{AA}^{01} in Eq. (19) for the calculation of the DOS of this system.

IV. RESULTS AND DISCUSSION

Using the present formulation, we have calculated the DOS for the one-dimensional muffin-tin alloy with a Markovian-type SRO. The expressions for various quantities, such as wave functions, scattering matrices, and the method of calculation of the path operators, are given in Ref. 21. Also given are the KKR-CCPA equations for a two-atom cluster. The lattice parameters (6.0 a.u.) and the muffin-tin radii (2.25 a.u.) of the two constituents of the alloy A_xB_y are taken to be identical. The depth of the potentials for the two constituents are taken as $V_0^A=0.3$ Ry and $V_0^B=0.5$ Ry, respectively.

In Figs. 1(a)–1(d), we present the results of our calculation for $x=0.1$ for various values of the SRO parameter α. Figure 1(a) shows the DOS for $\alpha=0.0$, which corresponds to the random alloy. In Fig. 1(b), we show the DOS for $\alpha=-0.11$, which is the minimum allowed value of α for $x=0.1$. We observe that the impurity band has become narrower and the structure around $E=0.06$ Ry

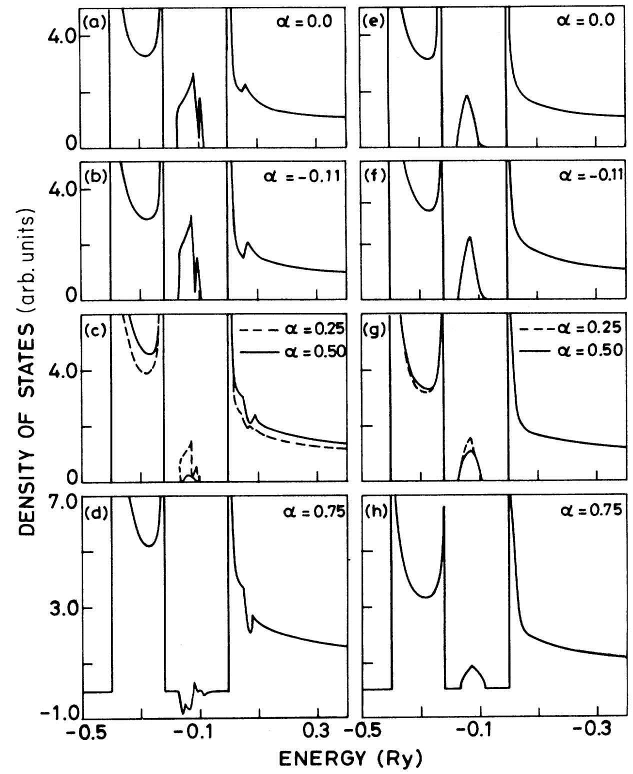

FIG. 1. Averaged density of states for the alloy with short-range order, for the concentration $x = 0.1$. The panels on the left-hand side (a)–(d) represent the results of the present method and those on the right-hand side (e)–(h) represent the results of the embedded cluster method (Ref. 15). Values of the SRO parameters are given in the legend.

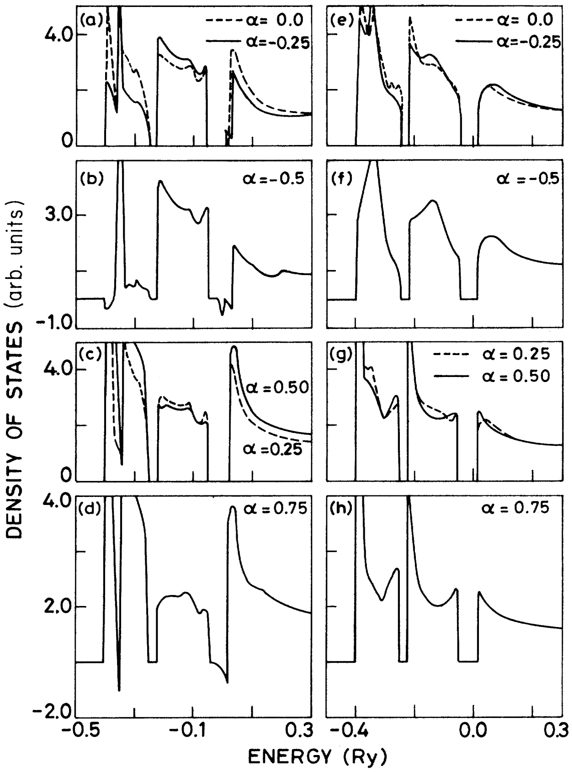

FIG. 2. Same as Fig. 1, but for $x = 0.5$.

has become sharper. In Figs. 1(c) and 1(d), we show the DOS for $\alpha = 0.25$ (dashed line), $\alpha = 0.50$ (solid line), and $\alpha = 0.75$. Here we see large changes in the DOS, particularly in the impurity band. We note that for $\alpha = 0.75$, the DOS becomes negative in the region between $E = -0.17$ Ry and $E = -0.09$ Ry. The values of α, for which the DOS is non-negative throughout the whole energy region, are from -0.11 to 0.50, and cover a wide range. We observe a general trend in these results. We note that as α increases gradually, some states from the impurity band are transferred to the first majority band. This is because when α increases, the probabilities of the *BB* and *AA* pairs increase, while those of the *AB* and *BA* pairs decrease. For $x = 0.1$, the probability of a *BB* pair is quite large compared to the other clusters. Hence, with the increase in α, the system tends towards a pure *B* system. Therefore, the DOS in the impurity band, which is due to *A*-type atoms, decreases. In Figs. 1(e)–1(h), we show the DOS obtained by the embedded cluster method of Gonis and Freeman[15] for various values of α. Also, in this case we observe that, with the increase in α, the impurity band loses some states, while the first majority band gains. Thus, there is a general agreement between the two results.

In Figs. 2(a)–2(d), we show the results of our calculation for $x = 0.5$ for various values of α. Again we see that the SRO introduces large changes in the DOS. We find that as α increases, some states from the second band are pushed into the first band. Also, we observe that the DOS remains non-negative for a considerably wide range of values of α (from -0.25 to 0.50) and becomes negative only when α is far away from its random limit. In Figs. 2(e)–2(h), we show the corresponding results calculated by the embedded cluster method.[15] We note that there is a general agreement between these results and the results obtained by our formulation.

It is clear from the above discussion that the approximation in which we have neglected the higher-order correction terms in the expansion of the configuration-averaged Green's function gives a non-negative DOS for a considerably wide range of the SRO parameter α. It gives a negative DOS only when α is very far from its value corresponding to the random system, in which case the higher-order terms in the expansion of the Green's function may become important. However, the values of α for most realistic systems[1–9] fall in the range of -0.30 to 0.20, for which our formulation yields a non-negative DOS at all energies. Moreover, it has been observed that a one-dimensional system is more sensitive than a three-dimensional system to the approximation, such as the one we have used.[14] Based on these considerations we feel that the present formulation will yield better results when applied to realistic alloys.

V. CONCLUSION

In this paper, we presented the generalization of the KKR-CCPA formalism to systems with SRO. We have used the generalized ASF to determine the configuration average of the site-diagonal form of the KKR Green's function, which turns out to be an infinite series expansion about its random average. We have shown that the expression for the configuration-averaged Green's function would yield a non-negative DOS at all energies. However, for numerical computations, we used an approximation in which the series was truncated after the second-order correction. We calculated the DOS for a one-dimensional muffin-tin alloy with Markovian-type SRO and found that the introduction of SRO can produce large changes in the DOS. We also found that this approximation yields a non-negative DOS for a considerably wide range of values of the SRO parameter.

ACKNOWLEDGMENTS

This work was supported by the Department of Science and Technology, New Delhi, India, through Grant No. SP/S2/M-39/87.

APPENDIX: PROOF OF HERGLOTZICITY OF $\langle G \rangle_{\mathrm{SRO}}$

The imaginary part of the configuration-averaged Green's function with SRO can be written as

$$\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} = \frac{1}{2i}[\langle G \rangle_{\mathrm{SRO}} - \langle G \rangle_{\mathrm{SRO}}^{\dagger}] , \tag{A1}$$

where $\langle G \rangle_{\mathrm{SRO}}^{\dagger}$ is the Hermitian adjoint of $\langle G \rangle_{\mathrm{SRO}}$. Using Eq. (5) in Eq. (A1) we get

$$\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} = \frac{1}{2i}\langle F|[\tilde{G}(\{M^i\})\tilde{\phi}(\{M^i\}) - \tilde{\phi}^{\dagger}(\{M^i\})\tilde{G}^{\dagger}(\{M^i\})]|F\rangle . \tag{A2}$$

In the discussions that follow, we will suppress the obvious functional dependence of $\tilde{G}$ and $\tilde{\phi}$ on $\{M^i\}$ because of convenience in writing. By simple algebraic manipulation, we get

$$\begin{aligned}\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} &= \frac{1}{2i}\langle F|\{\tilde{G}[\tilde{\phi}(\tilde{G}^{\dagger})^{-1} - (\tilde{G})^{-1}\tilde{\phi}^{\dagger}]\tilde{G}^{\dagger}\}|F\rangle \\ &= \langle F|\tilde{G}[-\mathrm{Im}(\tilde{G}^{-1}\tilde{\phi}^{\dagger})]\tilde{G}^{\dagger}|F\rangle .\end{aligned} \tag{A3}$$

From Eq. (2) we note that $\phi(\{n_i\})$ is a real and positive semidefinite function of $\{n_i\}$, and therefore, $\tilde{\phi}(\{M^i\})$ is a real and positive semidefinite functional of $\{M^i\}$. Thus, Eq. (A3) can be rewritten as

$$\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} = \langle F|\tilde{G}[-\mathrm{Im}(\tilde{G}^{-1})]\tilde{\phi}\tilde{G}^{\dagger}|F\rangle . \tag{A4}$$

From the definition of the Green's function, we get[34]

$$\tilde{G}(\{M^i\}) = [z\tilde{I} - \tilde{H}(\{M^i\})]^{-1} , \tag{A5}$$

where $\tilde{I}$ and $\tilde{H}(\{M^i\})$ are, respectively, the identity operator and Hamiltonian in the augmented space, and z is some complex number in the upper half-plane ($\mathrm{Im}z > 0$). It can be shown that[34]

$$\mathrm{Im}[\tilde{G}(\{M^i\})]^{-1} = (\mathrm{Im}z)\tilde{I} . \tag{A6}$$

From Eqs. (A4) and (A6) we finally get

$$\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} = -\langle F|\tilde{G}\tilde{\phi}\tilde{G}^{\dagger}|F\rangle(\mathrm{Im}z) . \tag{A7}$$

When there is no SRO, $\tilde{\phi} = \tilde{I}$, $\mathrm{Im}\langle G \rangle$ is negative definite, and Eq. (A7) gives the correct limit. Since $\tilde{\phi}$ is positive semidefinite, we can write $\tilde{\phi} = BB^{\dagger}$, where B is some operator in the augmented space. Thus, Eq. (A7) now becomes

$$\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} = -\langle F|(\tilde{G}B)(\tilde{G}B)^{\dagger}|F\rangle(\mathrm{Im}z) , \tag{A8}$$

which readily gives us

$$\mathrm{Im}\langle G \rangle_{\mathrm{SRO}} < 0 \text{ when } \mathrm{Im}z > 0 . \tag{A9}$$

Therefore, Eq. (5) and hence Eq. (8) will yield a non-negative DOS at all energies.

---

[1] S. C. Moss, J. Appl. Phys. **35**, 3547 (1964).

[2] L. H. Schwartz and J. B. Cohen, J. Appl. Phys. **36**, 598 (1965).

[3] C. R. Houska and B. L. Averbach, J. Appl. Phys. **30**, 1525 (1959).

[4] W. Lin, J. E. Sprueill, and R. O. Williams, J. Appl. Crystallogr. **3**, 297 (1970).

[5] C. E. Dahmani, M. C. Cadeville, J. M. Sanchez, and J. L. Moran-Lopez, Phys. Rev. Lett. **55**, 1208 (1985).

[6] J. Banhart, W. Pfeiler, and J. Voitlander, Phys. Rev. B **37**, 6027 (1988).

[7] K. Ohshima and D. Watanabe, Acta Crystallogr. A **29**, 520 (1973).

[8] J. Kulik, D. Gratias, and D. de Fontaine, Phys. Rev. B **40**, 8607 (1989); K. Ohshima, D. Watanabe, and J. Harada, Acta Crystallogr. A **32**, 883 (1976).

[9] P. S. Rudman and B. L. Averbach, Acta Metall. **2**, 576 (1954); F. A. Khwaja and M. S. K. Razmi, Phys. Status Solidi B **104**, 727 (1981).

[10] A. Bansil, in *Electronic Band Structure and its Applications*, edited by M. Yussouff (Springer-Verlag, Berlin, 1987), p. 273.

[11] J. S. Faulkner and G. M. Stocks, Phys. Rev. B **21**, 3222 (1980).

[12] H. Wright, P. Weightman, P. T. Andrews, W. Folkerts, C. F. J. Flipse, G. A. Sawatzky, D. Norman, and H. Padmore, Phys. Rev. B **35**, 519 (1987); D. van der Marel, J. A. Jullianus, and G. A. Sawatzky, *ibid.* **32**, 6331 (1985); N. Stefanou, R. Zeller, and P. H. Dederichs, Solid State Commun. **62**, 735 (1987).

[13] T. Kaplan and L. J. Gray, Phys. Rev. B **15**, 3260 (1977).

[14] L. J. Gray and T. Kaplan, Phys. Rev. B **24**, 1872 (1981).

[15] A. Gonis and A. J. Freeman, Phys. Rev. B **29**, 4277 (1984).

[16] A. N. Andriotis and J. E. Lowther, J. Phys. F **16**, 1189 (1986).

[17] F. J. Pinski, B. Ginatempo, D. D. Johnson, J. B. Staunton, G. M. Stocks, and B. L. Gyorffy, Phys. Rev. Lett. **66**, 766 (1991).

[18] A. Gonis and J. W. Garland, Phys. Rev. B **16**, 2424 (1977); A. Gonis, G. M. Stocks, W. H. Butler, and H. Winter, *ibid.* **29**, 555 (1984).

[19] O. K. Andersen, O. Jepsen, and M. Sob, in *Electronic Band Structure and its Applications* (Ref. 10), p. 1; J. Kudrnovsky and V. Drchal, Phys. Rev. B **41**, 7515 (1990).

[20] J. Banhart, H. Ebert, J. Voitlander, and P. Weinberger, Solid

State Commun. **65**, 693 (1988).

[21] S. S. A. Razee, S. S. Rajput, R. Prasad, and A. Mookerjee, Phys. Rev. B **42**, 9391 (1990).

[22] S. S. Rajput, S. S. A. Razee, R. Prasad, and A. Mookerjee, J. Phys. Condens. Matter **2**, 2653 (1990).

[23] S. S. A. Razee and R. Prasad, Phys. Rev. B **45**, 3265 (1992).

[24] S. S. A. Razee, Ph.D. thesis, IIT, Kanpur, 1991.

[25] A. Mookerjee, in *Electronic Band Structure and its Applications* (Ref. 10), p. 248.

[26] J. Callaway and N. H. March, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1984), Vol. 38, p. 135.

[27] For the proof of Eq. (2), the reader may refer to Ref. 14.

[28] For a detailed description of the states in the configuration space and an explicit form of M^i, refer to Refs. 21 and 23.

[29] See Eq. (12) of Ref. 23.

[30] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[31] J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

[32] G. L. Hall and J. Philhours, Phys. Rev. **139**, A160 (1965).

[33] P. C. Gehlen and J. B. Cohen, Phys. Rev. **139**, A844 (1965).

[34] S. S. A. Razee, A. Mookerjee, and R. Prasad, J. Phys. Condens. Matter **3**, 3301 (1991).