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Inclusion of charge correlations in calculations of the energetics and electronic structure for random substitutional alloys

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Currently, the coherent-potential approximation (CPA) implemented via the multiple-scattering theory of Korringa, Kohn, and Rostoker (KKR) gives the best first-principles description of the electronic structure for random substitutional alloys. However, the total energy has an important component of electrostatic energy missing, namely, that arising from the correlation of charges with varying atomic environments. We develop a "charge-correlated" CPA method (cc-CPA) which includes (some) local environmental charge correlations within the KKR-CPA method. We investigate the cc-CPA energetics for several alloys and show that the formation energies are in better agreement with experimental results. These calculations show that the excess charge on a species is almost completely screened by the first-neighbor shell. We then derive a simplified scheme to include the vast majority of the omitted electrostatic energy from charge correlations which requires only a species-dependent shift of the potentials within the original KKR-CPA method. We also discuss the ramifications on the electronic structure.

I. INTRODUCTION

The Korringa, Kohn, and Rostoker (KKR), multiple-scattering theory implementation of the coherent-potential approximation (CPA) has been highly successful in describing the electronic structure and other properties of random substitutional alloys (RSA). Historically, the CPA was developed for tight-binding models where the main interest was the effect of the random substitution on the electronic structure. Only after the CPA was combined with multiple-scattering theory could a density-functional theory of the total energy be developed for RSA.[1] For over a decade, calculations in many alloy systems have shown this method to do a good job in describing a variety of properties.[2] In spite of these successes, the KKR-CPA method has come under criticism because it improperly neglects (by construction) a possibly substantial electrostatic contribution to the total energy coming from the correlation of single-site charges due to the environment. Specifically, the charge density on an atom depends on the occupation of the atoms that surround it. The CPA, as a theory for obtaining configurational averages, assumes that every type of atom has the same charge density (i.e., the configurationally averaged), independent of a specific environment, and that each site on the underlying lattice is (charge) neutral on average. For ordered, binary alloys, Magri, Wei, and Zunger have shown that a charge on an atom is almost linear with the number of unlike neighbors in the first, near-neighbor (nn) shell.[3] Assuming this empirical relation holds for any type of local environment, such a correlation of charges with the nn environment leads to additional electrostatic energy in the random alloy that is not included within the standard CPA.[3] Here, we show how the effect of the correlation of charges with the local environment can be incorporated into the CPA so as to improve the description of the total energy of the random alloy. Moreover, the analysis of the first-principles results allows us to construct an analytic model to understand, for example, the charge distributions in the alloy and further simplify the method.

To be more explicit, we must first define a notation describing a random alloy and charge correlation. We define the usual site-occupation variable ξ_i to be 1 if the site i is occupied by an A atom, otherwise it is 0 for a B atom (we consider only the binary allow A_cB_{1-c} for simplicity). Thus, a random alloy is defined by a vanishing pair-correlation function for all $i \neq j$, namely,

$$\alpha_{ij} = \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle = c_i(1-c_i)\delta_{ij} , \tag{1}$$

where $c_i = \langle \xi_i \rangle$ is the average concentration of A atoms on the site i. The $\langle\ \rangle$ refer both to configurational averaging and to averaging over species.

Similarly, the electrostatic correlation energy is proportional to the charge-correlation function which is given by $\langle \Delta Q_{\alpha i} \Delta Q_{\beta j} \rangle - \langle \Delta Q_{\alpha i} \rangle \langle \Delta Q_{\beta j} \rangle$, where $\Delta Q_{\alpha i}$ denotes the excess charge on the site i for an α species. With Z_α the atomic number of an α species, this excess charge within a Wigner-Seitz cell, for example, is given by

$$\Delta Q_{\alpha i} = Z_\alpha - \int_{\mathrm{WS}} d^3 r_i \rho_\alpha(\mathbf{r}_i) . \tag{2}$$

The (imposed) charge neutrality of an alloy requires $\langle \Delta Q_{\alpha i} \rangle = 0$ for the effective one atom per unit cell case considered here. This neutrality condition forces the vanishing of the term $\langle \Delta Q_{\alpha i} \rangle \langle \Delta Q_{\beta j} \rangle$ inherent in the definition of the charge correlations. (We do not consider this term hereafter.) The electrostatic energy of interest is

$$E=\frac{e^2}{2}\sum_{i\neq j}\frac{\langle \Delta Q_{\alpha i}\Delta Q_{\beta j}\rangle}{|\mathbf{R}_i-\mathbf{R}_j|}\ . \tag{3}$$

For the (standard) single-site CPA, the configurationally averaged excess charges $\Delta Q_{\alpha i}$ are defined as $\Delta Q_A\xi_i+\Delta Q_B(1-\xi_i)$, with the $\Delta Q_{A(B)}$'s independent of the configurations $\{\xi_i\}$. Therefore, the energy from intersite charge correlations within the CPA vanishes since $\langle \Delta Q_{\alpha i}\Delta Q_{\beta j}\rangle$ is proportional to α_{ij}, which is zero for $i\neq j$. Beyond the requirement of uncorrelated site occupancies, an additional assumption has been imposed on the charge correlations within the CPA, namely the excess charge on a site is independent of configuration, as pointed out by Magri, Wei, and Zunger.[3]

In this paper, we derive a CPA method which includes these charge correlations (cc-CPA) in an approximate manner based on the assumption that the excess charge on a site is predominantly governed by the occupancy of only the nearest neighbor environment. We allow the charge on an atomic species to be a function of the number of unlike first neighbors. In a binary alloy, as a consequence of the above and the use of density-functional theory, each species has $N_{1\text{nn}}+1$ different charge densities, with $N_{1\text{nn}}$ being the number of first nearest neighbors; as a result the alloy system contains $2(N_{1\text{nn}}+1)$ components. For each atomic species the range of densities corresponds to the different nearest-neighbor environments. However, this does not require the excess charge to be a linear function. Remarkably, from the self-consistently determined charges densities for several random alloys, we find this function to be linear, in distinction to ordered alloys where it is almost linear. Moreover, the excess charge on an atom is almost proportional to the number of unlike first nearest neighbors with only a very small offset.

While the resulting approach is still an effective one atom per unit cell calculation, the parameter space for its solution is rather large and can lead to a large computational effort. To determine a simpler computational scheme we further investigate the consequence of the observed linearity in the model. We show that within the spirit of mean field, like the CPA, the cc-CPA can be reduced back to a two-component CPA but with a species dependent shift in the potentials that reflects effective charge screening in the random alloy due to charge correlations. We call this simplified model the screened CPA (scr-CPA). Our calculations of total energy based on the scr-CPA yields 85–95 % of the cc-CPA energy corrections.

For these new models, we have calculated the formation energies for a range of (fcc) $\text{Cu}_c\text{Zn}_{1-c}$ alloys, as well as the correction energies for (fcc) $\text{Cu}_{0.50}\text{Au}_{0.50}$ and (bcc) $\text{Ni}_{0.50}\text{Al}_{0.50}$ to examine trends. Compared to the standard KKR-CPA results, the cc-CPA and scr-CPA energies are shifted to lower values and are closer to experiment.

II. CHARGE CORRELATIONS IN A RANDOM ALLOY AND THE cc-CPA

In this section, we explore our model that incorporates charge correlations into a random substitutional binary alloy, A_cB_{1-c}, where $c_A=c$ and $c_B=1-c$ are the concentrations of A and B atoms. At this point, we emphasize that we are still considering a random alloy: every site has the same probability of being occupied by an A atom. However, as pointed out by Magri, Wei, and Zunger[3] the absence of correlation in the site occupations does not imply that charges of these atom are uncorrelated. By assuming that the charge density on an atom is a function of the number of unlike neighbors, we capture the major corrections. The binary alloy contains $N_{1\text{nn}}+1$ different charge densities for each species. The probability that a site is occupied by a species α and is surrounded in the first shell by n_A A atoms is

$$P^{\alpha}_{n_A}=c_\alpha B(N_{1\text{nn}},n_A)c_A^{n_A}c_B^{(N_{1\text{nn}}-n_A)}\ . \tag{4}$$

The function $B(N,n)=N!/n!(N-n)!$ is the usual binomial factor. Now consider $P^{\alpha\beta}_{n_An'_A}(s)$, the joint probability of having an α atom on site i surrounded in the first nn shell by n_A A's and of having a β atom on site j with n'_A A atoms in its first shell. The shell index s refers to the separation of sites i and j and designates the shell of which they are members. The form of $P(s)$ depends on this separation. For any neighbor beyond the fourth shell in fcc and the fifth in bcc, $P(s)$ factors into a product of single-site probabilities, since sites i and j have no shared nearest neighbors. (This is also true for the fourth shell in bcc.) The general form for a shell s is

$$P^{\alpha\beta}_{n_An'_A}(s)=c_\alpha c_\beta\sum_{n_1n_2n_3}B(m_1,n_1)B(m_2,n_2)c_A^{(n_1+n_2+n_3)}c_B^{(m_1+m_2+m_3)-(n_1+n_2+n_3)}\delta_{n_A,(n_1+n_2+\delta_{s1}\xi_j)}\delta_{n'_A,(n_2+n_3+\delta_{s1}\xi_i)}\ , \tag{5}$$

where m_2 is the number of nearest neighbors shared by sites i and j, n_2 of which are A's. The number of other atoms in the nearest-neighbor shell of sites i and j are given by m_1 and m_3, respectively, with the corresponding number of A atoms being n_1 and n_3. The parameters for fcc and bcc are given in Table I.

Having defined the single and joint probability functions, we may write the energy per atom due to charge correlations, as expressed in Eq. (3), as a sum over shells with distance R_s from the central site and N_s atoms per shell, i.e.,

$$\begin{aligned}E/N&=\frac{e^2}{2}\sum_s\frac{\langle \Delta Q_0\Delta Q_s\rangle}{R_s}\\&=\frac{e^2}{2}\sum_s N_s\sum_{\alpha n}\sum_{\beta n'}\Delta Q_{\alpha n}\frac{P^{\alpha\beta}_{nn'}(s)}{R_s}\Delta Q_{\beta n'}\ .\end{aligned} \tag{6}$$

TABLE I. For each neighbor shell s, the parameters m for the joint probability $P^{\alpha\beta}_{nn'}(s)$ given in Eq. (5) for a fcc and bcc Bravais lattice. For $s > 1$ the sites are not direct near neighbors and $m_1 + m_2$, or $m_2 + m_3$, equals the number of nearest neighbors; for $s = 1$, you must add the one direct neighbor to get the number of nearest neighbors.

	s	m_1	m_2	m_3		s	m_1	m_2	m_3
fcc	1	7	4	7	bcc	1	7	0	7
	2	8	4	8		2	4	4	4
	3	10	2	10		3	6	2	6
	4	11	1	11		5	7	1	7

For all shells where the joint probability can be factored, this average vanishes due to charge neutrality of the alloy. Note that this shows that long-range correlations are zero, and that the corresponding electrostatic energy has contributions from only a few near-neighbor shells. In contrast, for an ordered system, this electrostatic term has contributions from all shells, and is usually referred to as the Madelung energy. The corresponding shift in the potential for the species α with n A nearest neighbors is

$$\Delta V^{\text{cc}}_{\alpha n} = -\frac{e^2}{P^\alpha_n} \sum_{s\beta n'} N_s P^{\alpha\beta}_{nn'}(s) \frac{\Delta Q_{\beta n'}}{R_s} \ . \tag{7}$$

Note that these shifts are for the $(N_{1\text{nn}}+1)$ components in the alloy for each species α. The energy per atom can also be written in terms of these shifts, i.e.,

$$E/N = -\tfrac{1}{2} \sum_{\alpha n} P^\alpha_n \Delta Q_{\alpha n} \Delta V^{\text{cc}}_{\alpha n} \ . \tag{8}$$

Within this model of the excess site charges being only a function of the near-neighbor environment, Eqs. (7) and (8) represent an *exact* solution. To perform self-consistent, density-functional-based, electronic-structure calculations for random alloys, we must combine this electrostatic energy correction with the total-energy functional for the KKR-CPA, as derived by Johnson *et al.*,[1] generalized for $(N_{1\text{nn}}+1)$ components for each species α, of course. The $(N_{1\text{nn}}+1)$ potentials for each species are then determined variationally for this new total-energy functional, as done for the two-component CPA by Johnson *et al.*[1] We call this combination the charge-correlated CPA, or cc-CPA. This then completes the prescription for conducting a self-consistent calculation, albeit for a large number of components (which correspond to the different environments). For a fcc binary alloy, for example, we have 13 types of A atoms (as well as 13 B's).

An important point to make here is that we have not built any short-range order into the occupations, neither regarding the occupation of the variants of A's and B's nor of the A's and B's themselves. We have blurred the fact that the CPA is a theory for the random occupancy of sites by combining it with this correction. For example, the cc-CPA includes the arrangement where an A atom that we claim has all A nearest neighbors is sitting next to a B atom that we claim had no A nearest neighbors. Although this fictious arrangement is included with a small probability factor, it is hard to quantify the error in the energy and other physical quantities. In other words, we have not embedded a cluster nor have we done a cluster CPA. We are concentrating on the effects of charge correlations on the energy due to differing local environments only, which should be dominated by the omitted pieces of the electrostatics, not by the more subtle changes in the electronic structure due to averaging over particular types of physically realizable clusters.

In the past, such an idea has appeared for calculating the phonon spectrum in random alloys. Phonon frequencies, even for simple models, are poor if calculated within the standard (single-site) CPA because the CPA averages over all environments to get an "effective" force constant.[4] That is, the force between a particular atom on the central site and its neighbor is not well represented by this average. By including fluctuations in the diagonal elements due solely to differing near-neighbor environments, Whitelaw has found that the description of the photon spectrum is much better.[5] That work is similar in spirit to the approach taken here for electrostatic correlations. Unlike the charges, however, the force between two atoms does not depend on environment; but in both cases the environment is crucial in determining the physical properties. More recently, Nikolaev, Roth, and Vedyaev have reinvestigated how to obtain the electronic Green's function for a small cluster embedded into a CPA medium; that was used to study the same phonon model and found even better agreement to the exact results.[6]

III. RESULTS

The reason for the interest in charge correlations and their contribution to the energy is that they may contribute an appreciable amount of energy to the formation energies for the random alloys. Formation energy is one important quantity of interest when trying to understand phase stability, for example. Ultimately, calculating formation energies of ordered and disordered alloys within the same approach and code would allow rigorous comparisons. Here, we focus on the improvement of the formation energies of the random alloy for three fcc alloy systems, $\text{Cu}_{75}\text{Zn}_{25}$, $\text{Cu}_{50}\text{Zn}_{50}$, and $\text{Cu}_{50}\text{Au}_{50}$.

The fcc phase of Cu-Zn alloys is stable for Zn concentrations of less than 39%. The formation energies for a range of Cu-rich, random alloys are shown in Fig. 1. For comparison, we have plotted the old muffin-tin (CPA-MT) results of Johnson, *et al.*,[1] which underestimates the experimental formation energies by roughly 30%. The calculations using the atomic-sphere approximation (CPA-ASA) differ from experiment by roughly 18%. The cc-CPA-ASA results are indistinguishable from the experimental values.[7] Clearly, while the ASA changed the MT results for the better, the inclusion of the charge correlations provided a significant improvement.

The origin of long- and short-range order in the prototypical Cu-Au system is yet to be completely understood. We will not attempt this here, but show only the dramat-

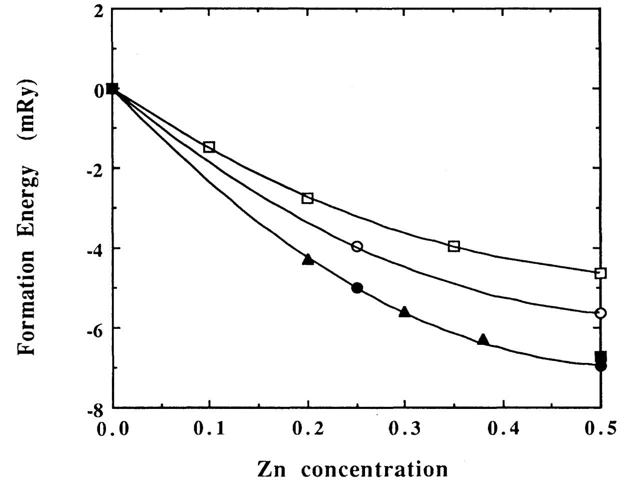

FIG. 1. The formation energy of disordered, fcc CuZn as a function of Zn concentration. Squares are muffin-tin results. All other results use the atomic-sphere approximation. Open circles are standard CPA, closed circles are charge-correlated CPA. Closed squares are screened CPA. Triangles are experimental values from Hultgren *et al.* (Ref. 7).

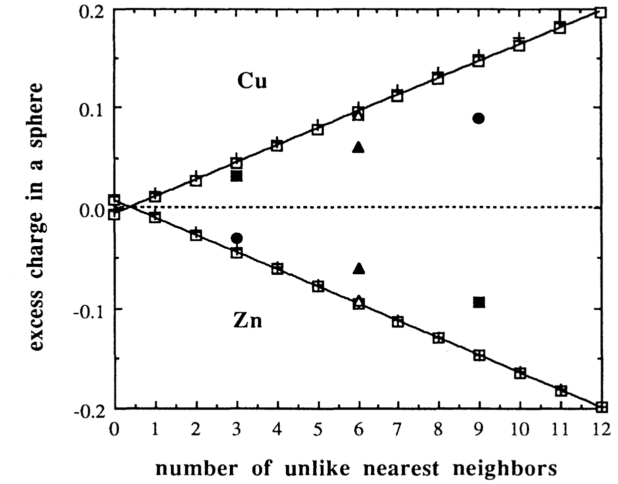

FIG. 2. The excess charges for atoms (in units of the electronic charge) which compose the charge-correlated CPA are plotted versus unlike nearest neighbors for fcc $Cu_{75}Zn_{25}$ (crosses) and $Cu_{50}Zn_{50}$ (open squares). The open triangles which intersect the lines are those obtained from the scr-CPA for 50% Zn. The closed squares, triangles, and circles are the results from standard CPA for 75%, 50%, and 25% Zn, respectively. The 25% Zn was not found for its equilibrium volume, but that of 50% Zn, which makes a small difference.

ic effect that these charge correlations can have on the formation energy of the random alloy. As shown below, the charges in $Cu_{50}Au_{50}$ are about twice that of CuZn alloys. Therefore, for the 50-50 alloy, the change from the standard CPA-ASA to the cc-CPA-ASA is roughly a factor of 4 larger for CuAu than for CuZn, i.e., −5.3 mRy versus −1.25 mRy, respectively. Keeping in mind that the ordering transition temperature in CuAu is 683 K, which is slightly larger than 4 mRy, this 5-mRy correction will be significant when describing the relative stability of the random phase.

The excess charges as a function of number of unlike nearest neighbors are shown in Fig. 2 for fcc $Cu_{75}Zn_{25}$ and $Cu_{50}Zn_{50}$ alloys at their respective equilibrium lattice constants. Besides a small offset at zero unlike neighbors, the plots are impressively linear. For the two, very different, concentrations, the plots lie almost on top of one another, which is an important confirmation of our underlying premise that the nearest-neighbor environment was of primary importance. The only reason the excess charges from the two concentrations are different is that global environments differ and this shows up in the offsets, as shown in the figure.

It is important to understand how the charges in the random alloy are distributed. The average charge on a central site occupied by an α atom is

$$\Delta Q_\alpha(0)=\sum_n P_n^\alpha \Delta Q_{\alpha n} \,. \tag{9}$$

In the alloy, when the charges are linear, the average excess charge $\Delta Q_\alpha(0)$ of a species is the excess charge of atom in the average environment. As for CuZn, we have found that the charges are linear functions for all alloys where we have used the cc-CPA. Now consider how the charges are distributed around $\Delta Q_\alpha(0)$. The effective charge per shell is defined as

$$\Delta Q_\alpha(s)=\frac{1}{c_\alpha}\sum_{n\beta n'} P_{nn'}^{\alpha\beta}(s)\Delta Q_{\beta n'} \,, \tag{10}$$

with the concentration prefactor required because the central site is definitely an α atom. In a random alloy with the charge on a site being determined by the nn local environment, this average charge per shell is only nonzero for the first-nearest-neighbor shell, because these are the only sites that are directly correlated with the central site. The sites in the other shells, although responsible for some of the correlation energy, are only correlated with the central-site charge indirectly through their mutual neighbors.

An example of our cc-CPA results, in random CuAu a $\Delta Q_\alpha(0)$ for the Cu site is +0.2058 electrons, whereas $\Delta Q_\alpha(s=1)$ is −0.2207 electrons. The offset found for Cu in CuAu is −0.0144 electrons. (For the Au site, these numbers are opposite in sign to four figures.) Note, if the offset were zero, then the first shell would completely screen the excess charge [simply subtract the offset from $\Delta Q_\alpha(0)$]. Of course, the individual sites in the random alloy are still neutral on average. For the Cu-Zn alloys, while the charges are comparable, the offset is an order of magnitude smaller and, therefore, the screening is more complete. This behavior of the average excess charge per shell $\Delta Q_\alpha(s)$ will be useful in returning to an effective, two-component CPA, as we show later.

In addition, the charges in an ordered calculation will be similar to that found in the cc-CPA for an equivalent environment. For CuAu, the standard CPA gave 0.14

and the cc-CPA gave 0.21 for the average excess charges. For the $L1_0$ structure, there is only one nearest-neighbor environment having 8 unlike neighbors. The excess charge found from the cc-CPA for this environment is 0.28 electrons. This is much closer to the 0.31 found in the ordered calculation.[8] To obtain ordered alloy energies, the charge densities from the cc-CPA are obviously better starting points for either starting self-consistent calculations or inserting into the Harris-Foulkes energy functions.[9] In addition, the electrostatic energy difference between the ordered and disordered states will be substantially smaller.

The single impurity limit provides another point of comparison. In Fig. 2, the standard CPA results can be extrapolated to give roughly a 0.12-electron charge deficiency of a zinc impurity in copper. This compares nicely to the value of 0.124 electrons found by the Zeller and co-workers calculation of a single-site, Zn impurity in bulk copper, where all charge densities remain fixed except for the density of the single impurity atom.[10] However, in an impurity calculation with the first-neighbor shell included in the self-consistency, the zinc has a deficit charge of 0.195 electrons. Almost perfect screening is achieved within the first shell which contains an excess charge of 0.204 electrons.[10] From the cc-CPA, we find a 0.199 charge deficiency of zinc with all unlike nearest neighbors. A similar charge effect is also seen in the calculations of impurities in nickel. Drittler *et al.* have remarked on their importance for determining the impurity formation energies.[10] Amazingly, the excess charges found in the cc-CPA provide fairly accurate values for the impurity limit, primarily due to their (almost) concentration independence, as noted above. Thus, the cc-CPA method yields central-site excess charges which have a certain amount of transferability across the entire concentration range.

IV. AN ANALYTIC MODEL

Clearly our results show that the excess charge is proportional to the number of unlike near neighbors except for a small offset. In this section, we investigate the ramifications of forcing the excess charge to be strictly proportional to the number of unlike nearest neighbors, and then show the effect of the offset. With zero offset, one can ask (and *algebraically* answer) several questions. What is the shift in the total energy? Magri, Wei, and Zunger, have answered this question for a random fcc alloy.[3] A more detailed question is, given that a site i is occupied by an α atom, what are the average charges on various shells $\Delta Q_\alpha(s)$? This average shell charge vanishes for all but the first-neighbor shell where, surprisingly, it is equal in magnitude but opposite in sign to the excess charge at the central site, independent of the Bravais symmetry. Analytically, when a nonzero offset is included, the average charge on the first shell no longer exactly screens the excess charge on the central site, as found in the self-consistent results.

To see how these results arise, we let the excess charge $\Delta Q_{\alpha n}$ be given by $-a_0+\lambda(N_{1\mathrm{nn}}-n)$ for a central-site A atom and $b_0-\lambda n$ for a central-site B atom, where n refers to the number of A atoms in the first shell. This represents the linear dependence on number of unlike nearest-neighbor atoms with an offset. Charge conservation $[\sum_\alpha c_\alpha \Delta Q_\alpha(0)=0]$ in the alloy requires that $c_A a_0$ equals $c_B b_0$. Using the definition of the effective charge per shell, Eq. (10), and charge neutrality, one can show with a little algebra that $\Delta Q_A(s=1)$ equals $-\lambda(N_{1\mathrm{nn}}-\bar{n})$, which is $-\Delta Q_A(0)$ shifted by a_0. Here, $\bar{n}$ is the average number of A atoms, which is $c_A N_{1\mathrm{nn}}$; it defines the average environment and thereby the average charge. Thus, with an offset there is no longer perfect screening. An example of this effect was given in the cc-CPA results above. The resulting expression for the energy within this little model can be derived similarly and it has contributions in all shells where the joint probability distribution cannot be factored, even though these average shell charges vanish.

V. MEAN-FIELD THEORY OF CHARGE CORRELATIONS: THE scr-CPA

We can simplify the procedure defined by Eqs. (7) and (8) to make it more amenable for use when it is combined with the KKR-CPA. Specifically, in Eq. (8), let $\Delta Q_{\alpha n}$ become independent of n by replacing it by the averaged excess charge on an atom, i.e., $\Delta Q_\alpha(0)$. We then obtain a mean-field approximation to the electrostatic energy correction, which can be written (per atom) as

$$\Delta E^{\mathrm{scr}} \approx \frac{e^2}{2}\sum_{\alpha s} c_\alpha \frac{\Delta Q_\alpha(0)\Delta Q_\alpha(s)}{R_s} = -\frac{e^2}{2}\sum_{\alpha} c_\alpha \frac{\Delta Q_\alpha(0)^2}{R_1} , \tag{11}$$

since $\Delta Q_\alpha(s)$ is always zero for $s>1$ and is $-\Delta Q_\alpha(0)$ for $s=1$. When added to the CPA, this mean-field approximation returns us to the two-component CPA but with an additional shift in the potentials of

$$\Delta V_\alpha^{\mathrm{scr}} = e^2 \frac{\Delta Q_\alpha(0)}{R_1} . \tag{12}$$

Thus, in a random alloy, an atom on a central site experiences an average, effective-potential field which perfectly screens, by the first-neighbor shell, the excess charge of that atom. If, at the outset, we let the charges be independent of environment, as in the CPA approach, this effective field is zero. The effective field is nonzero due to the environmental dependence of the charges, where we have explicitly accounted for only nearest-neighbor correlations. Recently, Abrikosov *et al.*, have used this potential shift[11] and based its use on the empirical evidence from impurity calculations.[10] However, their energy correction differs from Eq. (11) by a factor of 2, which is due to a double-counting error.

We refer to the method with this mean-field correction included into the CPA electronic-structure approach as the screened CPA, or scr-CPA. The scr-CPA includes a majority of the charge correlations that were pointed out as missing from the standard CPA. Just as importantly, the scr-CPA consistently makes the same approximations for the configurational averaging of the energy associated with charge correlations as it does for the configurational averaging of the electronic structure. From this viewpoint, it is best thought of as a mean-field approximation for the energy associated with screening of charges in a perfectly random alloy, and, in distinction to the cc-CPA, there is then no inconsistency of having not embedded a cluster into a CPA medium to determine all electronic properties.

What are we missing in this approximation? We are forgetting, for example, about the restriction that a central-site A atom, which has all A nearest neighbors, cannot have a B in the first shell. Or, for a more complicated example, a central-site atom having all A nearest neighbors cannot have a second near-neighbor atom which has all B nearest neighbors. In Eq. (8) such terms are handled by the joint probability distribution. This approximation also forces perfect screening by the first-neighbor shell, and, therefore, does not allow any small offset.

The excess charges within the scr-CPA are found to be very close to those calculated in the average environment in the cc-CPA calculations. For example, in $\mathrm{Cu_{50}Au_{50}}$, we find ΔQ_{Cu} to be 0.198 for the scr-CPA and 0.206 electrons for the cc-CPA. The standard CPA gave 0.131 electrons for ΔQ_{Cu}. Note the -0.014 offset in the cc-CPA (in the linear relationship of the charge with the number of unlike nearest neighbors) is the same size as the difference between the scr-CPA and cc-CPA charges but opposite in sign. This has been seen in all the cases investigated so far. As expected, the scr-CPA excess charges are very close to those of the average environment in the cc-CPA, and larger than those from the standard CPA.

How realistic are these offsets found in the cc-CPA? There is no reason to think that an offset cannot exist. A cluster of like atoms in a random alloy does not have to be neutral, as found in the impurity calculations.[10] This offset could reflect this fact. The offsets could also be a consequence of one of the approximations, such as not really embedding a cluster in the CPA; the cc-CPA model makes an error in the electronic band-structure effects. Whether those offsets we find are real or an artifact of the model we cannot answer at this point. If the charges in the scr-CPA were shifted by a small offset, it would do little to change the energy. In the cc-CPA, the contributions to the energy in some shells beyond the first are not insignificant, but are opposite in sign.

Albeit more approximate than the cc-CPA, the scr-CPA has the advantage that its implementation is no more difficult than the standard CPA. We have used this scr-CPA to calculate the same formation energies as discussed above and find that the scr-CPA captures at least 85–95 % of the cc-CPA correction to the single-site CPA total energy. As shown in Fig. 1 for equiatomic CuZn, the scr-CPA gets 95% of the correction. For equiatomic CuAu, scr-CPA gets 89% of the correction, 4.7 mRy out of 5.3 mRy. Finally, an even more dramatic correction is found in the bcc NiAl system, which is strongly ordering. The energy shift from the standard CPA is 7.7 mRy. Previous muffin-tin-type calculations for the "ordering energy" (i.e., the energy difference between the disordered CPA and order $B2$ states) for bcc NiAl found a major discrepancy with an estimate from experiment.[12] While the large correction in NiAl found here explains a significant portion of that discrepancy, the improvements made by using the ASA in the electronic-structure calculations, specifically to obtain the Hartree contributions to energy, will certainly be of some importance. This is under investigation for both the fcc and bcc Ni-Al alloys.

The 5–15 % discrepancy between the scr-CPA and the cc-CPA arises from the neglect of the charge correlations in the energy beyond the mean-field and, to a lesser extent, the small offset charge found in the cc-CPA. Unless these electrostatic energy corrections are the order of 10 mRy, as in NiAl alloys, then the scr-CPA should be adequate for energetics. If more details about the distributions of charges, moments, etc., are required, then this information can only be obtained from the cc-CPA.

The large charge-correlation energy in NiAl is predominantly due to the larger excess charges in the system (which is commonly, albeit erroneously, referred to as larger "charge transfer"). Of course, the definition of excess charge is not unique. This is the common problem within any calculation because there is not a unique assignment of space to particular atoms. Within density-functional treatments, the standard CPA has but one Wigner-Seitz cell size. Therefore, for any atom embedded in the CPA medium, this cell defines the volume associated with that atom. Here, we are approximating the polyhedral cell as a sphere which maintains the overall volume constraint, i.e., the atomic-sphere approximation.

We note, however, that it is occasionally the practice within ordered calculations which use the ASA to utilize the extra degree of freedom, namely, the ratio of sphere sizes of the different types of atoms, to minimize the energy or make the cells neutral (which many times are equivalent).[13] Even though there is no variational statement regarding this procedure, this is done so as to improve agreement with experiment or full-potential calculations. We wish to comment on this procedure when applied to CPA calculations, especially since an adjustment of the scr-CPA to make each cell neutral seems attractive because it would make the potential shift zero. For the standard or screened CPA which determine configurational averages via an effective atom approach, the adjusting of sphere sizes is, in general, a physically incorrect procedure. This is because the configurationally averaged Hartree energy is determined from effective A- and B-type atoms which when made neutral, for example, does not reflect the true distribution of charges on atoms in varying local environments and, therefore, the energy drops to some unphysical value.[14] To be specific, there are some environments with an A atom surrounded by all A's and it is roughly neutral already without adjusting its sphere; while an A surrounded by all B's would have to have its sphere radius severely adjusted. Each of these possibilities occur with some probability and they have to be properly averaged to get the Hartree energy, for example. The effective atom approach within the standard or screened CPA cannot perform this average correctly by adjusting the sphere of the effective atoms. As a matter of practice, if the excess charges are very small, such a procedure may yield reasonable results, but, in general, this is not reliable. For the cc-CPA, which takes into account the varying environments and varying probabilities, such a procedure would be similar to ordered calculation and may improve the description of energetics compared to, say, a full-potential approach; however, the additional degrees of freedom in the calculation make the approach rather unwieldy, even though the sphere radii can be roughly estimated from plots like those in Fig. 2.

VI. DISCUSSION

There remains some additional points to address in regards to the two new approaches discussed here. Namely, with all the past successes using the standard KKR-CPA method in describing electronic structure and associated properties, what modifications to the electronic structure is found using these cc-CPA or the scr-CPA? We have calculated the density of states and the spectral functions (i.e., Fermi surface) for $Cu_{50}Zn_{50}$ and $Cu_{50}Au_{50}$ by all three methods. We have not provided a plot of these quantities because there is little discernible differences between the three methods. This is not to say there are not any differences; there are small shifts due to changes in charge transfer, etc. At this time, we just have not found any physical properties that are unduly affected by these differences.

Second, there remains some outstanding issues regarding how to improve the description of the electrostatic correlation energy in "full-potential" methods. Clearly, there is no question that a single unit cell may be better described by a potential that does not use a shape approximation; however, this does not address how to incorporate the correlations discussed here. It is not obvious how one generalizes these simple arguments and ideas to a case which is not highly symmetric. For example, higher-order multipole effects from the nearest-neighbor screening may be of the same order as those coming from eliminating the shape approximation on the central site. Without a better foundation, it is not clear that a full-potential CPA will improve the description of the random alloy over the ASA. (Of course, here we are only discussing metallic alloys or systems without highly directional bonds.)

The two methods discussed here have advantages over other approximate treatments of the electronic structure of random alloys, such as the so-called special quasirandom structure (SQS) method.[15] For example, for nonoverlapping, environmentally independent, point charges the electrostatic corrections to the random alloy energy is zero, as is found in the current model and the standard CPA. This is not so of the SQS which uses successively larger ordered unit cells to represent a random alloy by approximating the zero site correlation functions; in that case, it is a nonmonotonically, slowly convergent approximation for the electrostatic energy. Also, even for a binary alloy, the number of atoms in the ordered unit cell is large, making these types of calculations more computational intensive than the effective one atom per cell calculations in the CPA methods.

Furthermore, the extension of either the cc-CPA or scr-CPA to handle ternaries, or a general *n*-component alloys, can be easily done and without the concomitant increase in the computational effort needed for the SQS. The extension of the cc-CPA is based on the premise that the charge on an atom depends only on the number of *like* nearest neighbors, regardless of what *unlike* atoms occupy the other sites in the shell. The scr-CPA can then be derived by the same factorizations, with the only change for the standard CPA being the additional terms in the energy and the potentials, given by Eqs. (11) and (12). In addition, the extension to a multisublattice CPA can be obtained similar to the completely random case by determining the proper joint probabilities for a given sublattice occupancy and following the above arguments.

No one local environment in an alloy can fully screen an excess charge on an atom. In a random alloy, only through the configurational averaging do we obtain the local screening described above. For an ordered alloy, there is only one local configuration and it does not locally screen any excess charges. Starting from the high-temperature, random alloy, these short-ranged, charge correlations (which locally screen the excess charges) become longer and longer ranged until, at the ordering transition, they extend throughout the alloy. The region in which the screening takes place follows this correlation length. Upon ordering, the long-ranged, electrostatic energy is commonly referred to as the Madelung energy. This local screening in the random alloy had not been included in previous methodologies of the KKR-CPA, but, in either of the methods described here, they have been included in an approximate way. The cc-CPA has the advantage of describing a range of environments seen in the alloy. And, as we have seen, this includes the impurity limit due to the almost concentration independence of the excess charge as a function of environment. This implies that the charges from the cc-CPA posses a certain amount of transferability across the entire concentration range and confirms the underlying premise that the nearest neighbor environment is of primary importance. The calculations are complicated, however, since the number of components and computational requirements grow. (The computational growth is linear in the number of components since it is due mostly to calculations of the wave functions.) The scr-CPA returns the calculational method to the simplicity of a single charge density for each component, reproduces the average excess charge found in the cc-CPA, and retains most of the energy correction. The improved agreement with experiment has shown the usefulness of these methods.

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[1] D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Gyorffy, and G. M. Stocks, Phys. Rev. B **41**, 9701 (1990); Phys. Rev. Lett. **56**, 2088 (1986).

[2] For example, see various contributions, in *The Electronic Structure of Complex Systems,* edited by P. Phariseau and W. M. Temmerman (Plenum, New York, 1984); also, *Alloy Phase Stability,* Vol. 163 of *NATO Advanced Study Institute, Series E: Applied Science,* edited by G. M. Stocks and A. Gonis (Klewer, Dordrecht, 1989).

[3] R. Magri, S.-H. Wei, and Alex Zunger, Phys. Rev. B **42**, 11 388 (1990).

[4] H. W. Diehl and P. L. Leath, Phys. Rev. B **19**, 596 (1979).

[5] D. J. Whitelaw, J. Phys. C **14**, 2871 (1981).

[6] M. Yu. Nikolaev, L. M. Roth, and A. V. Vedyaev, Phys. Rev. B **46**, 7358 (1992).

[7] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Glesier, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Binary Alloys* (American Society of Metals, Metals Park, OH, 1973), p. 818.

[8] D. Seifu, W. A. Shelton, F. J. Pinski, D. D. Johnson, and G. M. Stocks (unpublished).

[9] J. Harris, Phys. Rev. B **31**, 1770 (1985); W. M. C. Foulkes (unpublished); Ph.D. thesis, Cambridge University, 1988; also, W. M. C. Foulkes and Rodger Haydock, Phys. Rev. B **39**, 12 520 (1989).

[10] For a Zn impurity in Cu, R. Zeller (unpublished); R. Zeller, J. Phys. F **17**, 2123 (1987); and, N. Stefanou, A. Oswald, R. Zeller, and P. H. Dederichs, Phys. Rev. B **35**, 6911 (1987); B. Drittler, M. Weinert, R. Zeller, and P. H. Dederichs, Phys. Rev. B **39**, 930 (1989).

[11] I. A. Abrikosov, Yu. H. Vekilov, P. A. Korzhavyi, A. V. Ruban, and L. E. Skilkrot, Solid State Commun. **83**, 867 (1992).

[12] W. A. Shelton, D. M. Nicholson, G. M. Stocks, F. J. Pinski, D. D. Johnson, and P. Sterne, in *Alloy Phase Stability and Design,* edited by G. M. Stocks, David P. Pope, and Anthony F. Giamei, MRS Symposia Proceedings No. 186 (Materials Research Society, Pittsburgh, 1991) pp. 113–122; also G. M. Stocks, W. A. Shelton, D. M. Nicholson, F. J. Pinksi, G. Ginatempo, A. Barbieri, B. L. Gyorffy, D. D. Johnson, J. B. Staunton, P. E. A. Turchi, and M. Sluiter, in *Ordered Intermetallics—Physical Metallurgy and Mechanical Behavior,* Vol. 213 of *NATO Advanced Study Institute, Series E: Applied Science,* edited by C. T. Liu, *et al.* (Kluwer, Dordrecht, 1992), pp. 15–36.

[13] We are not aware of any papers that explicitly address this point, but it is known among practitioners.

[14] D. D. Johnson (unpublished).

[15] Alex Zunger, S.-H. Wei, L. G. Ferreira, and James E. Bernard, Phys. Rev. Lett. **65**, 353 (1990).