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Applicability of the coherent-potential approximation in the theory of random alloys

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The applicability of the coherent-potential approximation (CPA) for the description of electronic properties of completely random alloys is investigated. This is done by calculating the density of states and the total energy for different systems and by comparing the results with those obtained for large supercells consisting of up to 320 atoms in the framework of the order-N locally self-consistent Green's function method. Thereby it is found that in the framework of the CPA one obtains a reliable description of the electronic structure of random alloys. The total energy of a completely disordered alloy can also be reliably estimated provided an appropriate account is given for the electrostatic contribution to the one-electron potential and energy. Therefore, we conclude that the CPA can be safely applied to study the influence of disorder on various properties of metallic alloys for which the muffin-tin or atomic sphere approximation is sufficient and the chemical contribution to the total energy dominates. [S0163-1829(98)03122-1]

I. INTRODUCTION

The coherent-potential approximation (CPA), originally introduced by Soven[1] for the electronic structure problem and by Taylor[2] for phonons in random alloys, has become one of the most popular techniques to deal with substitutional disorder. The success of the CPA is to a large extent associated with its formulation in the framework of the multiple scattering theory given by Györffy.[3] Combined with the Korringa-Kohn-Rostoker (KKR) basis set or the linear muffin-tin orbital (LMTO) basis set, the CPA has been used for calculations of bulk electronic structure,[4] ground state thermodynamic properties,[5–15] phase stabilities,[16–21] magnetic properties,[22–29] surface electronic structure,[30–33] segregations,[34–37] and many other characteristics of alloys.

However, it is very difficult to control the error of the coherent-potential approximation. If one derives the CPA formally as an expansion of the Green's function for a disordered system,[38–41] it is possible to show that the corresponding series contains all diagrams describing electron scattering by a single site to infinite order. However, there is no small parameter in such an expansion, which allows one to judge the applicability of this approximation. A small parameter, the ratio between the concentration and the coordination number c/Z, has been proposed based on an intuitive argument.[41] A comparison with simple analytical models cannot clarify the problem. The result of such a comparison can neither completely justify nor disprove an approximation because as a rule these models have very little in common with the situation in real materials. So far the success of the CPA has been measured mostly by comparisons between theory and experiment, which, though impressive, can sometimes be misleading. First, it is known that negative results are seldom presented in the literature. Second, the experimental information is obtained for alloys that almost always exhibit short-range-order effects, neglected in the CPA. On the other hand, it is also very difficult to compare CPA calculations with other theoretical methods, such as Connolly-Williams[42] or special quasirandom structure (SQS) method[43,44] with small SQS's. Recently, it has been shown that the mixing energies of random fcc Al-Ag (Ref. 45) and Ag-Au (Ref. 46) alloys obtained from CPA calculations, the Connolly-Williams method, and the SQS methods agree well with each other provided one uses similar approximations among these methods. However, there are examples where the agreement is not as good,[44] but it is not clear *a priori* which of the methods is more accurate than the other. Therefore, there exist some doubts about the reliability of the results obtained within the CPA.[44,47–49]

In the present paper we will compare the electronic density of states and the total energies of random substitutional alloys between different metals calculated within the coherent-potential approximation and by the recently proposed locally self-consistent Green's function (LSGF) method.[50,51] The LSGF method is an order-N method for calculation of the electronic structure of systems with an arbitrary distribution of atoms of different kinds on an underlying crystal lattice. It is shown to be particularly suitable for the investigations of random alloys that are modeled by large periodic supercells with several hundreds of atoms in the unit cell. The order-N scaling is achieved by associating each atom in the system with its so-called local interaction zone (LIZ).[52,53] Inside each LIZ the multiple scattering problem is solved exactly. The accuracy of the LSGF calculations is controlled by the size of the LIZ and its minimal size is ensured by embedding the LIZ into a self-consistent mean-field CPA-like effective medium. For the simplest case of the single-site LIZ, the LSGF is almost equivalent to the CPA for a multicomponent alloy (with a number of components equal to the number of atoms in the supercell) and the only difference is a correct (in the framework of the atomic sphere approximation) account of the electrostatic contribution to the one-electron potential and the total energy of an alloy in the LSGF method. Therefore, it is clear that the LSGF allows us to treat a random alloy problem better than the CPA. Because of this and also because all other computational details (i.e., basis set, local density approximation, etc.) will be essentially equivalent in the CPA and LSGF calculations, a comparison between their results is meaningful and the difference, if it occurs, must be directly attributed to errors of the CPA.

II. ANALYSIS OF ASSUMPTIONS UNDERLYING THE CPA

In order to understand the critical comments that have been made in the literature on the CPA (Refs. 44 and 47–49) and problems for which the comparison with more advanced theoretical method have to be made, we will first repeat an analysis of the basic assumptions behind the coherent-potential approximation. A complete discussion can be found in Ref. 4. We will consider a completely random binary alloy A_cB_{1-c} with only one type of disorder, the substitutional disorder. This means, in particular, that there exists an underlying crystal lattice and the sites of this lattice are occupied by the alloy components with probabilities equal to their concentrations. The occupation of each site does not depend on whether neighboring sites are occupied by A or B atoms, i.e., there is no short-range order in the alloy. Though the size mismatch of alloy components can cause different interatomic distancies to be different, i.e., so-called local relaxation effects, we will not take these effects into consideration. We remark that such local relaxations can influence the results for the density of states and the total energy calculations in some cases of very large size mismatches.[44] However, the recent systematic study of lattice relaxations around a single impurity in Cu by Papanikolaou *et al.*[54] has shown that this contribution to the impurity solution energy in general is small compared to the values calculated earlier without lattice relaxations.[49] Based on the results of these two papers, we leave the investigation of the relaxation problem beyond the scope of the present paper. Finally, any complications due to partial ordering will not be considered, though these effects could easily be included in the CPA (Ref. 13) as well as in the LSGF (Ref. 51) calculations.

The key quantity in the calculation of electronic and thermodynamic properties of solids is the one-electron Green's function and the CPA is an approximation for calculating its average value in random alloys. In this approximation a real system is replaced by an ordered lattice of effective scatterers. The properties of these effective atoms have to be determined self-consistently by the condition that the scattering of electrons off real atoms embedded in the effective medium vanishes on the average. In the atomic sphere approximation (ASA) and within the LMTO basis set,[55–59] this condition is written as

$$\tilde{\mathbf{g}} = c\mathbf{g}^A + (1-c)\mathbf{g}^B, \tag{1}$$

where g is the so-called KKR ASA Green's function, the tilde refers to the effective medium, bold symbols denote a matrix in LL', L being the combined angular-momentum quantum numbers (l,m), and $\mathbf{g}^{i=(A,B)}$ are Green's functions of the alloy components embedded into the effective medium. The latter are given by the solution of the single-site Dyson equation

$$\mathbf{g}^i = \tilde{\mathbf{g}} + \tilde{\mathbf{g}}(\tilde{\mathbf{P}} - \mathbf{P}^i)\mathbf{g}^i. \tag{2}$$

In Eq. (2) P^i and $\tilde{P}$ are potential functions for the alloy components and for the effective atoms, respectively.[55–59,33]

The success of the CPA in comparison with other single-site approximations [virtual crystal approximation (VCA) or average t-matrix approximation (ATA)] is determined by Eq. (1), where the averaging is performed on the self-averaging quantity, that is, the one-electron Green's function. On the contrary, neither the one-electron potential that is averaged in the VCA nor the t matrix in the ATA has a property of self-averaging. Despite this fact, a comparison of the CPA spectra with models that can be solved either analytically or by computer simulations, for example, the random binary alloy model,[40] has revealed the following trends. The CPA gives a very good description of the alloy density of states if the separation between the energy levels of the alloy components is not too large. If this is not the case the CPA density of states turns out to be much smoother than the ''exact'' results, that is, sharp peaks that occur for the latter are almost totally smeared out for the former. In other words, the CPA should not work well for the systems with a split band behavior.

There is also a concern related to the accuracy of Eq. (2). First, in the conventional CPA for a two-component alloy one always assumes that if a particular site is occupied by an atom A (B), then the potential function determined by the corresponding one-electron potential for this site is P^A (P^B). Any variations of these functions due to local environment of the chosen site are neglected. On the other hand, calculations that goes beyond the single-site approximation, for example, by the so-called embedded cluster method[60] or using SQS's,[44] have shown that the density of states changes drastically for atoms of the same kind but with different local surroundings. The net charges of alloy components also depend strongly on the number of unlike nearest neighbors.[44,7,61] Recently, an effect of these charge fluctuations has been observed experimentally as a disorder broadening of the core electron photoemission spectra.[62] As a result one should expect substantial variations of the potentials and potential functions between the chemically equivalent atoms; it is not clear to what extent these variations are unimportant. In particular, it was suggested[44] that some fine structure of the density of states that is present in real random alloys is destroyed due to the neglect of these fluctuations. Second, the application of the single-site Dyson equation for the problem of a single impurity in an ideal host[49] resulted in a substantial error for the calculated impurity solution energies. Though recently Ruban and Skriver[63] have shown that to a large extent this situation is improved by the proper use of the single-site approximation, the question about the reliability of this approximation itself still remains.

Another problem is the calculation of the electrostatic contribution to the alloy one-electron potential and total energy. As a matter of fact, the CPA determines a way of calculating the average one-electron Green's function for a given potential, but does not provide a prescription of how to calculate this potential.[64] In practice, of course, starting with the work of Winter and Stocks[65] self-consistent one-electron potentials were calculated in the framework of the CPA and an expression for the alloy total energy was justified.[6] However, the Madelung contribution to the alloy potential and energy was not included. Moreover, it is not possible to take this effect into account completely within the single-site approximation and one needs to go beyond the mean-field approximation when calculating the alloy electronic structure in order to understand the nature of the electrostatic interactions in random alloys and to suggest a reasonable model for the Madelung potential and energy that can be used in the framework of the CPA. At present this problem is widely discussed in the literature from the theoretical[47,48,9–15,7,61,64,66,67,46] and experimental[62] points of view. For example, Faulkner *et al.*[61,64] have performed an analysis of the electrostatic potential and energy in random Cu-Zn and Cu-Pd alloys modeled by very large supercells. They have found a nontrivial functional relation between the net charge on site and Coulomb potential at site, the so-called qV relation. They also introduced a model for the Coulomb energy. Unfortunately it is too complicated to be directly applicable for CPA calculations. Magri *et al.*[47] and Lu *et al.*[48] examined the Madelung energy in random metallic alloys on the basis of calculations for ordered compound. They found that the net charge on an atom in a metallic alloy depends linearly on the number of its nearest unlike neighbors and used this fact to formulate a simple model for charge correlations in alloys. A similar conclusion was obtained by Johnson and Pinski[7] on the basis of calculations for random alloys in the framework of the charge-correlated (CC) CPA. These authors suggested a mean-field version of the CC CPA, the so-called screened CPA model. Recently, this type of model has been generalized to account for more distant correlations by Wolverton *et al.*[67] A different approach to the problem allowed Korzhavyi *et al.*[12,9,11,13] to formulate the screened impurity model (SIM).

This model is based on the empirical observation that the net charge on an impurity atom in a metallic matrix is almost completely screened by the net charges of its nearest neighbors.[68] Based on this, there are two simple assumptions behind the SIM. First, the net charge of an alloy component $Q_{A(B)}$ embedded in the effective CPA medium is completely screened by the first shell of effective atoms that surround it. This assumption must not be confused with screening of net charges of real atoms in real alloys. The SIM deals with the restricted average net charge for the A or B component of the alloy. Second, the screening charge is uniformly distributed among all nearest neighbor atoms. The corresponding Madelung contribution to the one-electron potential is then given as

$$V_M^{A(B)} = -e^2 \frac{Q_{A(B)}}{R_1}, \tag{3}$$

where R_1 is the radius of the first coordination shell, e is the electron charge, and the net charge $Q_{A(B)}$ is defined as

$$Q_i = \int_{S_{WS}} d^3r\ \rho_i - Z_i . \tag{4}$$

In Eq. (4) the integral is taken over the atomic sphere, defined by the radius S_{WS}, and Z_i and ρ_i are the atomic number and the electron density of component i, respectively. The expression for the Madelung energy may then be written

$$E_M = -\beta e^2 c(1-c)\frac{(Q_A-Q_B)^2}{R_1}. \tag{5}$$

Surprisingly, all the models mentioned above, except that of Refs. 61 and 64, may be reduced to formula (5) with different prefactors β.[12] The prefactor β cannot be defined exactly within the CPA. In Refs. 12 and 13 it was demonstrated that even though a single value of β can be chosen for all concentrations and values of lattice parameters, it varies from system to system. However, this conclusion was made on the basis of a comparison with experiment or with calculations using the Connolly-Williams method and therefore is not completely reliable. Also in the model of Faulkner *et al.*[61,64] the Madelung energy consists of two terms. The first (denoted as u_{C1}) corresponds to Eq. (5) with $\beta = 0.5$. The second term (u_{C2}) describes the contribution to the Coulomb energy due to local environment fluctuations and cannot be directly calculated within the CPA. However, the ratio of these two terms may be viewed as a measure of the deviation of β from 0.5,

$$\beta = 0.5 + u_{C2}/2u_{C1}. \tag{6}$$

In Eq. (6) we have used the fact that in Refs. 61 and 64 the ''effective'' radius for the Cu-Zn alloy was found to be very close to the radius of the first coordination shell [R_1 in Eq. (5)]. From the results presented in Ref. 64 one can see that in general u_{C2}/u_{C1} depends on the system and concentration, but it is not clear to what extent this dependence influences the total and the electrostatic energy of an alloy. Again, more systems have to be tested because, as a matter of fact, there is no other simple suggestion except three mathematically equivalent models, the SIM, the screened CPA, and the charge-correlated model, on how to calculate the Madelung energy and potential in random alloys in the framework of the CPA.

III. COMPUTATIONAL DETAILS

In order to make a comparison between the CPA and the supercell LSGF calculations as meaningful as possible we have used essentially the same computational setup in both cases. All calculations were performed by means of the scalar relativistic LMTO method in the tight-binding representation employing s,p, and d orbitals in conjunction with the atomic sphere approximation.[55–59] Exchange and correlation were included within the local-density approximation using the Perdew-Zunger parametrization[69] of the many-body calculations of Ceperley and Alder.[70] During the self-consistent procedure the reciprocal space integrals were calculated by means of 280–540 k points in the irreducible part of the bcc or fcc Brillouin zone, while the energy integrals were evaluated on a semicircular contour in the complex energy plane using 16–25 energy points distributed in such a way that the sampling near the Fermi level is increased. When calculating the density of states (DOS) we increased the number of k points by an order of magnitude. The Green's function was evaluated for 1000 points on a line in the complex energy plane parallel to the real axis and was then analytically continued towards the real axis.

In our LSGF calculations we model a random alloy by means of a supercell consisting of 144 atoms for fcc alloys and 128 atoms for bcc alloys. Inside the supercell the atoms are distributed in such a way that the pair correlation functions are zero up to the sixth shell of nearest neighbors, which ensures a very good convergence of the total energy and the alloy density of states with respect to the supercell size.[51] However, in some cases larger supercells with up to 320 atoms were considered. In Refs. 50 and 51 it was also shown that the convergence of the total energy calculations by the LSGF method with respect to the size of the local interaction zone is particularly good for the random alloys and as a rule a single-site LIZ is sufficient to obtain an accuracy of the order of 0.1 mRy. However, to eliminate possible artificial agreement between the CPA and the LSGF calculations we have used the LIZ that includes up to four shells of neighboring atoms. In addition, this ensures very good convergence of the calculated site-decomposed DOS. The total DOS was found to converge already for much smaller, in general, single-site LIZ sizes.

IV. RESULTS AND DISCUSSION

A. Density of states for a completely random alloy

Let us start the discussion by considering the question of how well the CPA describes the density of states for binary random fcc alloys when the separation between the band centers of the alloy components increases. For this purpose we have considered three Cu-based alloys on the fcc crystal lattice, Cu-Pd, Cu-Au, and Cu-Zn. These systems have been extensively studied in the framework of the CPA (Refs. 71–80, 13, 5, and 6) and the supercell approaches.[81,44,61,64] Here they are chosen for a reason that becomes clear from Fig. 1. In this figure we show the distribution of the number of atoms having particular values of the LMTO band center parameters C (Refs. 55–59) as obtained from our LSGF calculations for 144 atom supercells. One observes that the Cu-Pd system exhibits a common band behavior, while a separation between the bands increases through the Cu-Au alloy towards the Cu-Zn alloy, which is already definitely a case with well separated bands. In addition, there are significant variations of the potential parameters for the same alloy components in all alloys, thereby allowing us to check the accuracy of the CPA with respect to this effect.

In Fig. 2 we show the density of states for the $Cu_{50}Pd_{50}$ alloy. The total density of states calculated in the framework of the CPA and that for the supercell by the LSGF method are indistinguishable from each other [Fig. 2(a)]. The same conclusion can be made for the restricted averages of the DOS calculated for each alloy component separately [Fig. 2(b)]. To illustrate the fact that the observed agreement is not just an artifact of using a CPA-like effective medium in our LSGF calculations we show in Fig. 2(c) the DOS for several atoms in the supercell that have different local environments. One can clearly identify a substantial difference between, say, a Pd atom that has 11 unlike nearest neighbors and one with just 3 of them and similar effects for the Cu atoms. However, when averaged in the total alloy density of states, the result become essentially the same as that obtained by the CPA mean-field treatment.

As a matter of fact, this agreement should be expected for alloys with common band behavior. Therefore, the case of the Cu-Au alloy represents a more interesting example, as the separation between the Cu and Au bands increases when compared to Cu-Pd. However, we remark that in the Cu-Au system a band splitting is still smaller than the bandwidth.

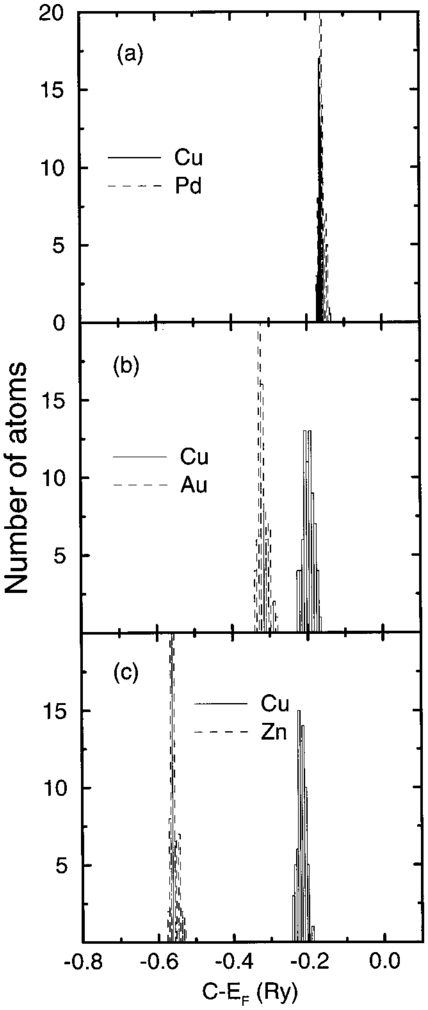

FIG. 1. Distribution of the number of atoms having certain values of the LMTO band center potential parameter C in the 144 atom supercells modeling random equiatomic fcc (a) Cu-Pd, (b) Cu-Au, and (c) Cu-Zn alloys. The data for Cu are shown by the full line, the data for the other alloy components are shown by the dashed lines.

The total densities of states for the $Cu_{75}Au_{25}$ alloy calculated by the two methods is again shown in Fig. 3(a), while the corresponding restricted averages are given in Fig. 3(b). We have chosen this particular composition due to a very interesting effect discussed earlier in the literature. Namely, an ordered Cu_3Au alloy shows well pronounced peaks in the low-energy Au-related part of the spectrum that are completely washed out in the random alloy calculated by the scalar-relativistic CPA. It was also shown that the peaks are associated with Au atoms completely surrounded by Cu neighbors.[78,44] As such a configuration must be present in a real random alloy, the traces of the peaks could survive, and the too smooth DOS calculated by the CPA for the Au part of the spectrum has been viewed as a failure of this approximation.[44]

In Fig. 3(c) we show that, indeed, the DOS for an Au atom surrounded by only Cu neighbors in the two first shells exhibits a sharp atomiclike virtual bound state originating from the fact that there is almost no Cu d electrons in this energy interval and therefore there is no site available for the Au d electrons to hop to. However, due to the low probabil-

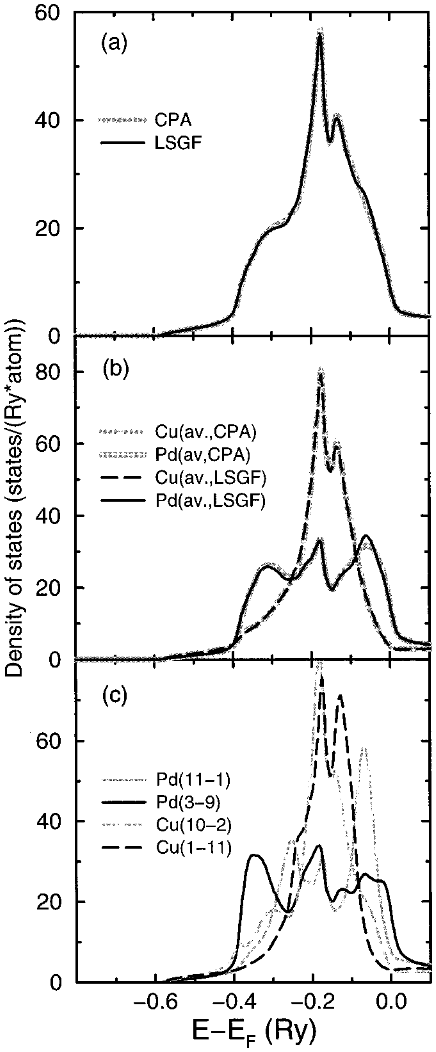

FIG. 2. Density of states of the random fcc $Cu_{50}Pd_{50}$ alloy. The (a) total DOS and (b) restricted average DOS were calculated for a 144 atom supercell by the LSGF method (thin black lines) and in the framework of the CPA (thick gray lines). In (b) the restricted average DOS for Cu is shown by dashed lines and for Pd by solid lines. In (c) the site decomposed DOS calculated by the LSGF method for several atoms having different numbers of unlike (the first number in parentheses) and like (the second number) nearest neighbors is shown.

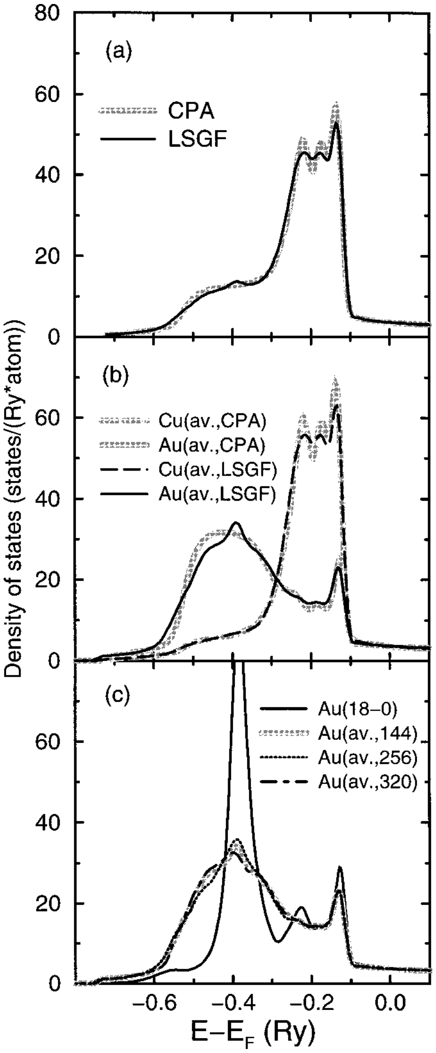

FIG. 3. Density of states for the random fcc $Cu_{75}Au_{25}$ alloy. The notation in (a) and (b) is similar to that in Fig. 2. In (c) the DOS for the Au atom having 18 Cu neighbors in the first two shells is shown as a full black line. The restricted average DOS for the Au calculated for supercells with 144 (full gray line), 256 (dotted black line), and 320 (dot-dashed black line) atoms is also shown in (c).

ity of this configuration to occur in a random alloy, this peak is hardly seen in the restricted average of the DOS for Au in the alloy, which turns out to be in good agreement with the CPA result [Fig. 3(b)]. Even better agreement is observed for the total density of states [Fig. 3(a)] because of the relatively low concentration of Au in the $Cu_{75}Au_{25}$ alloy. In addition, we show in Fig. 3(c) the average DOS for Au in this alloy, calculated by the LSGF method for supercells of different sizes. Very good convergence is clearly seen.

In this respect it is interesting to analyze what would be the response of the density of states of Cu-Au alloys to a change of concentration. If the Au concentration decreases, the relative probability to find an Au atom completely surrounded by Cu neighbors increases and vice versa if the Au concentration increases. Therefore, we expect that the agreement between the total DOS, calculated by the CPA and the LSGF, will be again very good. This is really the case, as one can see in Figs. 4(a) and 4(b), where we present a comparison of the DOS calculated for fcc $Cu_{90}Au_{10}$ and $Cu_{50}Au_{50}$ alloys by these two methods. However, as one can see in Fig. 4(c), the average local density of states for Au atoms in the $Cu_{90}Au_{10}$ alloy calculated in the framework of the CPA deviates from the result obtained by the LSGF method for a 256 atom supercell. We will explain this deviation later, but we would like to point out that our result is in agreement with the earlier observation made by Ruban and Skriver,[63] who also found that the CPA predictions for total average quantities, such as the total energy or the total density of states, are more reliable than predictions of restricted averages. In fact, the coherent-potential approximation was formulated to calculate total averages in random alloys and one has to keep this in mind in actual applications.

Finally, let us consider the Cu-Zn system.[84] As one can see from Fig. 5, the separation between the Cu and Zn *d* bands is of the order of the bandwidth and this is a case where a comparison between the CPA and the ''exact'' re-

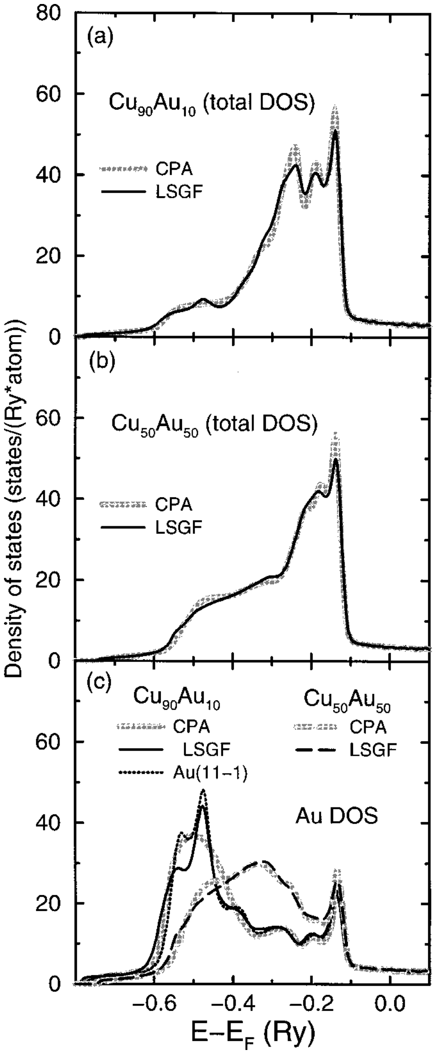

FIG. 4. Density of states for the random fcc (a) $Cu_{90}Au_{10}$ and (b) $Cu_{50}Au_{50}$ alloys calculated for 256 atom supercells by the LSGF method (thin black lines) and in the framework of the CPA (thick gray lines). In (c) the restricted average DOS for Au atoms is shown by solid lines ($Cu_{90}Au_{10}$) and dashed lines ($Cu_{50}Au_{50}$). The DOS for an Au atom in $Cu_{90}Au_{10}$ alloy surrounded by 1 Au and 11 Cu nearest neighbors is shown in (c) by black dotted line. It has been obtained by the LSGF method.

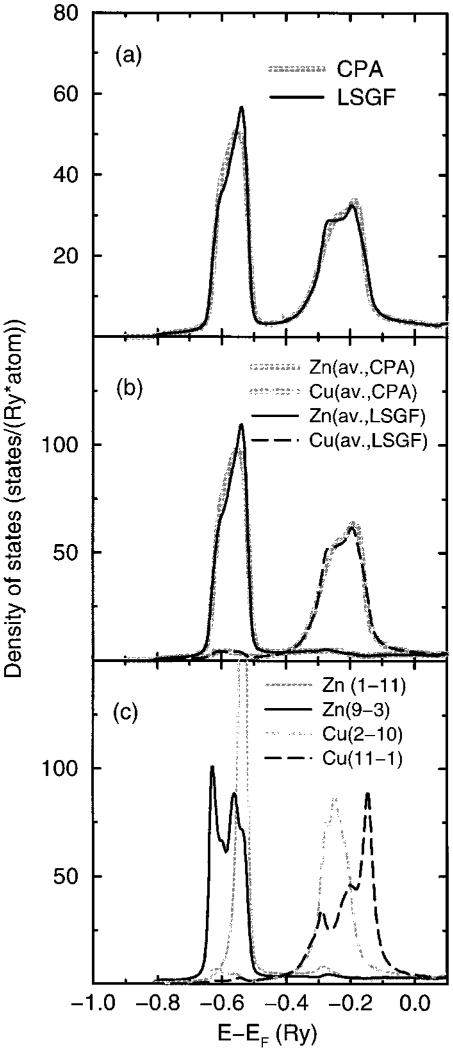

FIG. 5. Density of states for the random fcc $Cu_{50}Zn_{50}$ alloy. The notation is similar to that of Fig. 2.

sults for the simple analytical models shows large discrepancies.[40] Thus the CPA is supposed to fail for the Cu-Zn system. However, as a matter of fact, it does not and the agreement between the mean-field and the supercell results is again very impressive for both the total DOS [Fig. 5(a)] and the DOS averaged over the alloy components [Fig. 5(b)]. In Fig. 5(c) we show again the density of states for the different atoms in the supercell, which allows us to explain why the CPA in fact works in this case. The point is that in the models it is customary to consider only two levels for the two alloy components. In the case of a large separation between them, the model DOS has sharp peaks, smeared out by the CPA due to the fact that its mass operator is complex. However, the situation when at least one of the alloy components has well defined energy level could occur only in dilute alloys. Indeed, in our calculations for the fcc $Cu_{90}Au_{10}$ alloy we have found that the *restricted average* of the Au DOS is almost totally dominated by the DOS for the Au atom surrounded by 1 Au and 11 Cu nearest neighbors [compare the full and the dotted lines in Fig. 4(c)]. In this case the situation is very similar to what has been observed in model calculations, namely, that the CPA smears out the fine structure of the DOS. This, however, is not seen in the *total* DOS due to the dilution effect. On the other hand, in alloys with higher concentrations the energy levels of the alloy components have different locations due to the different local environments of each atom [see Figs. 1(c) and 5(c)] and as a result the DOS is smeared out and is in almost perfect agreement with the CPA DOS. It is amusing to notice that due to the existence of fluctuations of the local potentials for the same alloy component, which is supposed to work against the applicability of the CPA, they turn out to contribute to its accuracy.

B. Total energy of a completely random alloy

From the discussion above one can judge the accuracy of the description of the electronic structure of random alloys in the framework of the coherent-potential approximation. However, as has been pointed out in Sec. II, calculations of the self-consistent potentials and total energies are additionally complicated by the inability to account for the electro-

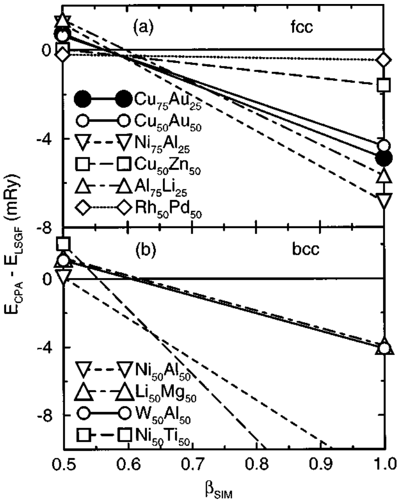

FIG. 6. Total energies of different (a) fcc and (b) bcc random alloys calculated in the framework of the CPA and the screened impurity model (SIM) as a function of the SIM parameter β relative to the LSGF total energies calculated for the same alloys modeled by 144 atom (fcc) and 128 atom (bcc) supercells.

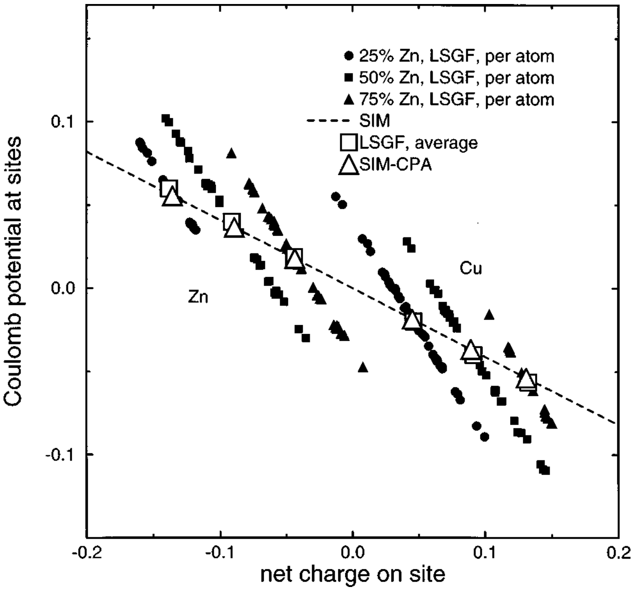

FIG. 7. Coulomb potential at a site as a function of the net charge on site for three fcc Cu-Zn alloys [25% (filled circles), 50% (filled squares), and 75% (filled triangles) of Zn] calculated by the LSGF method. Values to the left are for Zn and those to the right are for Cu. Averaged values are shown by open squares. The dashed line shows the qV relations as expected from the SIM and the corresponding average values calculated self-consistently in the framework of the SIM CPA are shown by the open triangles. A fixed Wigner-Seitz radius $R_{WS}=2.70$ a.u. was used for all alloys.

static potential and energy of disordered systems within the CPA. In the present paper we will concentrate on the practical part of this problem, namely, we will try to understand if it is possible to describe in practice the total energy of a random alloy within the very simple screened impurity model (see Sec. II). This will be done by considering a large number of different examples.

The main problem is that, unfortunately, the parameter β of the model cannot be determined within the framework of the CPA itself. Therefore, in order to obtain β it has been suggested in Ref. 13 to use other methods of total energy calculations for random alloys that do not rely on the single-site approximation. The LSGF method is very suitable for this purpose. There are several questions that must be answered. First of all, one may investigate whether there exists a single value of the parameter β in Eq. (5) that gives satisfactory results in different systems. At this point let us emphasize that we will compare *total* energies obtained by different techniques rather than the *electrostatic* contribution to the total energy as has been done in earlier studies of random alloys with the help of large supercells.[61,64,67] Our reasons for this are the following. First, it is the total energy that is the quantity of main interest in most calculations. Second, we have found that the total energy converges faster with respect to the size of the supercell than its separate contributions (including the Madelung energy). This allows us to use medium size supercells (between 100 and 200 atoms) in our studies. However, there is also the second question that arises in this context, namely, whether Eq. (5) with β obtained from a comparison with other first-principles methods really describes the Madelung energy of a random alloy or whether it compensates both kinds of errors coming from the unknown part of the Coulomb energy and the CPA itself.

To answer the first question we have compared total energies, calculated by the LSGF method for different alloys (modeled again by large supercells) and in the framework of the SIM CPA for different values of the prefactor β. The so-obtained energy differences are shown in Fig. 6 as a function of β for fcc [Fig. 6(a)] and bcc [Fig. 6(b)] alloys composed from different elements. We observe that for the former all lines crosses the zero line (i.e., results of the SIM CPA become equivalent to those of the LSGF supercell calculations) at about the same value of the parameter $\beta=0.6$. Of course, there could be examples where the agreement would not be so good, but so far we have not yet found such a case. It appears, therefore, that for the close-packed fcc structure there exists a universal value of $\beta=0.6$, which allows one to calculate the total energy of a completely random alloy in the framework of a mean-field treatment almost with the same accuracy as with a method that goes beyond the single-site approximation. For the more open bcc structure we find larger discrepancies between the optimal β values in different alloys due to the larger role of the screening from the second shell of nearest neighbors. Still $\beta\sim0.6$ is a rather good choice. The ordering energies calculated within the CPA for the Ni$_{50}$Ti$_{50}$ and Ni$_{50}$Al$_{50}$ alloys are -30 and -36 mRy, respectively, and the error compared to the reference LSGF calculations (-32 and -38 mRy) is only of the order of 2 mRy, or about 5% of the ordering energy itself. In any case, without taking the electrostatic contribution into consideration these values become -46 and -45 mRy, respectively, i.e., the error increases substantially.

The second question has already been discussed in the literature in Refs. 64 and 46, where it was found that Eq. (5) with $\beta=0.6$ gives a satisfactory, though not perfect, description of the Madelung energy at least in Cu-Zn (Ref. 64) and Ag-Au (Ref. 46) alloys. In Figs. 7 and 8 we illustrate directly how well Eqs. (3) and (5) work. In Fig. 7 we have presented the qV relations[61,64] obtained by our LSGF calculations for 144 atom supercells which model the completely random

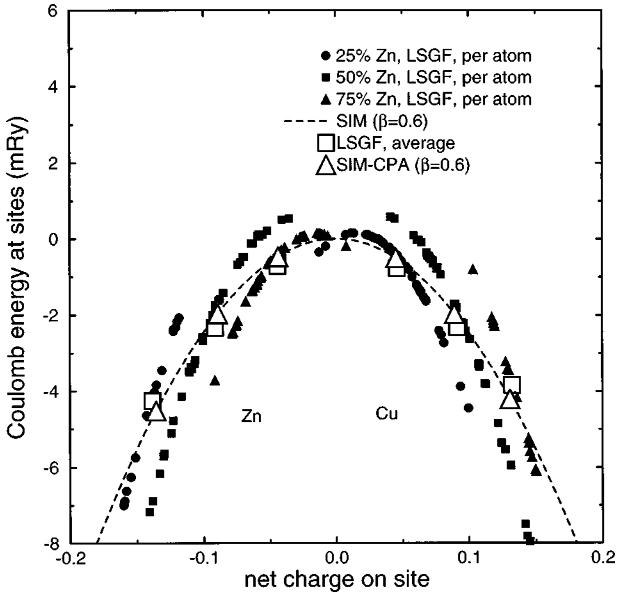

FIG. 8. Coulomb energy at a site decomposed into atomic sphere contributions as a function of the net charge on the site for the same fcc Cu-Zn alloys as in Fig. 7. The notation is similar to that in Fig. 7.

fcc Cu-Zn alloy at three stoichiometric compositions: 25% (circles), 50% (squares), and 75% (triangles) of Zn. Though we have used smaller supercells compared to the calculations reported in Refs. 61 and 64, the slopes of the lines in our calculations and in these works agree well with each other. Also in Fig. 7 we show a line, calculated from Eq. (3) (dashed line). One can see that its slope differs from those of the qV relations and this disagreement is to be expected because the SIM has been suggested as a model to calculate average values of the electrostatic contributions to the one-electron potential and energy. When one consider average values for the alloy components, calculated by the SIM CPA (open triangles in Fig. 7) and the LSGF (open squares), very good agreement is found. Notice also the very good agreement between not only potentials, but also average net charges in the CPA and the supercell calculations. This adds to our belief in the reliability and internal consistency of the SIM because net charges were calculated self-consistently in the framework of the SIM CPA and in principle did not have to be the same as in the reference LSGF calculations.

Similar conclusion can be drawn from Fig. 8, where we plot the Coulomb energy at a site calculated in the ASA as a function of the net charge on the site for three fcc Cu-Zn alloys: $Cu_{75}Zn_{25}$, $Cu_{50}Zn_{50}$, and $Cu_{25}Zn_{75}$. Here we make use of the ASA decomposition of the alloy Madelung energy into site contributions E_M^i for each site i in the supercell

$$E_M^i = \frac{1}{2} Q_i V_M^i . \tag{7}$$

This partitioning is not physical, but it allows us to compare the LSGF results with those of the SIM CPA, where a similar partitioning of the restricted averages of the Madelung energy for the A or B alloy components have the form[12]

$$E_{A(B)} = -\beta e^2 \frac{Q_{A(B)}^2}{R_1} . \tag{8}$$

A parabolic shape of the curves presented in Fig. 8 is to be expected from the qV relations. Again, one can see several branches for different concentrations and the SIM expression (8) with $\beta = 0.6$ (dashed line in Fig. 8) does not fall exactly on them. However, the average values again agree very well between the CPA and the supercell calculations. It appears therefore that the SIM with universal prefactor $\beta = 0.6$ can be used together with the CPA technique to obtain a reasonable ASA estimate of the energy of random alloys.

However, we remark that the SIM includes only the monopole-monopole contribution to the electrostatic potential and energy. Therefore, it is supposed to be used only in connection with the muffin-tin (MT) approximation or ASA. In view of the complications that arise in setting up a model for this contribution we expect it would be even more complicated to take into account other nonspherical terms and consequently to arrive at a generalization of the CPA to the case of the full potential or full charge density methods. However, Koepernik *et al.*[82] recently applied basic ideas of the SIM in order to estimate the electrostatic potential in their linear combination of atomic orbitals CPA calculations. Also Korzhavyi and Ruban[83] have found that in certain cases SIM CPA ASA calculations can reproduce the results of the LSGF calculations, which include nonspherical corrections to the ASA. In the latter case, of course, neither $\beta = 0.6$ nor the screening radius in Eqs. (3) and (5) remains universal. However, we believe that a consistent way of treating this problem is to go beyond the single-site approximation and to use other methods, for example, the LSGF (Refs. 50 and 51) or the locally self-consistent multiple-scattering method.[52,53,61,64]

V. SUMMARY

We have compared results for the density of states and the total energy of completely random alloys in the framework of the coherent-potential approximation with those obtained for large supercells by the order-N locally self-consistent Green's function method. As the LSGF goes beyond the single-site approximation, but keeps all other computational aspects essentially the same as in the CPA, such a comparison allows us to check precisely the applicability of this approximation in the theory of random alloys. For the density of states very good agreement was observed for three alloy systems, Cu-Pd, Cu-Au, and Cu-Zn, despite the fact that the separation between the band centers increases from Pd to Au and from Au to Zn, and there are substantial variations in the potentials for the same alloy components having different local environments. We show that a reliable estimate of the alloy total energy may be obtained within the CPA. We also find that in the atomic sphere approximation and in the framework of the screened impurity model there exists a universal prefactor of this model $\beta = 0.6$, which gives satisfactory agreement between the CPA and the LSGF total energies in all systems considered in the present study.

However, we note that there are several aspects of the CPA that were not considered in the present work and limit its applications. Among those are the inability of the CPA to treat nonspherical contributions to the one-electron potentials, which makes it hardly possible to set up a meaningful full-potential version of the method, the inability to treat consistently local lattice relaxations, and the inability to describe directly the short-range-order effects in alloys. However, our results strongly suggest that the CPA can be safely applied to study the influence of disorder on various properties of metallic alloys for which the MT or the atomic sphere approximation is sufficient and the chemical contribution to the energy dominates over several other contributions, for example, elastic, vibrational, and due to many-electron effects. Fortunately, the above-mentioned criteria are fulfilled for a large group of problems in most alloys between transition metals or between transition and simple metals. To study more sensitive phenomena, for example, short-range-order effects,[50] one must, of course, go beyond the single-site approximation. This can be done, for instance, in the framework of the LSGF method, used here to provide reference data.

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