PHYSICAL REVIEW B **70**, 064203 (2004)

# Electronic structure calculations on alloys using the polymorphous coherent-potential approximation

S. Pella and J. S. Faulkner
*Alloy Research Center, Department of Physics, Florida Atlantic University, Boca Raton, Florida 33431, USA*

G. Malcolm Stocks and Balazs Ujfalussy
*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA*

(Received 6 January 2004; revised manuscript received 22 April 2004; published 20 August 2004)

We present self-consistent calculations of the electronic density of states of disordered copper-palladium and silver-palladium alloys using the polymorphous coherent-potential approximation and the Korringa-Kohn-Rostoker coherent-potential approximation. We find that the agreement between the theoretical partial density of states of palladium *d* bands in copper-rich copper-palladium alloys and experiment is significantly improved when the polymorphous coherent-potential approximation is used. The densities of states of silver-palladium alloys calculated with the two versions of the coherent-potential approximation are identical and agree with experiment. This indicates that the improved treatment of Coulomb effects in the polymorphous coherent-potential approximation is necessary only for alloys such as copper palladium that have considerable charge transfer.

DOI: 10.1103/PhysRevB.70.064203 PACS number(s): 71.23.−k, 71.20.Be

## I. INTRODUCTION

Calculations of the electronic density of states (DOS) for disordered copper-palladium (Cu-Pd) alloys using the Korringa-Kohn-Rostoker (KKR) coherent-potential approximation (CPA)[1,2] are not in agreement with the experimental data. This is in contrast with the excellent predictions made by the KKR-CPA calculations on silver palladium (Ag-Pd) alloys.[3] In this paper we present self-consistent polymorphous coherent-potential approximation (PCPA) calculations of the DOS in Cu-Pd and Ag-Pd alloys, and compare the results with KKR-CPA calculations on the same alloys and with experiment.

Discrepancies between the Cu-Pd DOS calculated with KKR-CPA and that measured using ultraviolet photoemission spectroscopy (UPS)[4] were attributed to shortcomings of the theory, particularly to the placement of the atoms on the sites of the ideal Bravais lattice in the KKR-CPA model. Later photoemission spectroscopy measurements using synchrotron radiation took advantage of the Cooper minimum in the Pd 4*d* photoelectron cross section to separate the spectra into the contributions from the Pd and Cu atoms in the alloy.[5] These measurements show that the partial spectral weight (PSW) for Cu agrees with the Cu DOS calculated with the KKR-CPA, but the calculations overestimate the number of states observed in the lower-energy range of the Pd PSW. Several possible interpretations were offered for this discrepancy, but the one emphasized in later experimental studies is the effect of atomic displacements from the sites of the Bravais lattice.[6] It was shown that agreement with experiment could be obtained with KKR-CPA calculations that are not charge self-consistent by the simple expedient of shifting one of the potentials.[7] Other non-self-consistent KKR-CPA calculations improved the agreement by including atomic displacements in an approximate way.[8]

More recently, XPS and UPS studies of the electronic structure of Cu-Pd have been carried out using synchrotron radiation.[9] As in the previous studies, the Pd PSW's in the soft x-ray regime seem very different from the predictions of the KKR-CPA, but a more careful analysis demonstrates that the main reason for this discrepancy is not the failure of the theory but the result of strong matrix-element effects that obscure the accurate determination of the Pd DOS in the bonding state region. The improvement in the agreement between the experimental results and the KKR-CPA calculations is dramatic, but there is still a discrepancy that we show in this paper can be reduced even further by using the PCPA rather than the KKR-CPA.

A short description of the major differences between the KKR-CPA and the PCPA is presented in Sec. II. In Sec. III, we give some of the details of the KKR-CPA and PCPA calculations for the DOS of Cu-Pd and Ag-Pd disordered alloys. We discuss the implications of these calculations in Sec. IV.

## II. THE KKR-CPA AND THE PCPA

Theories for the electronic states of alloys make use of the density functional theory (DFT) and local density approximation (LDA),[10] which subsumes the many-electron interactions into a one-electron potential. For the special case of substitutional solid-solution metallic alloys, which are the subject of this paper, it is normally assumed that the atoms in an alloy with the composition $A_cB_{(1-c)}$ reside on the sites of a periodic Bravais lattice. The probability for an $A$ atom being found on a specific site is $c$, and the probability for the $B$ atom being there $1-c$. The Wigner-Seitz cells $\Omega_i$ centered on the lattice points $\mathbf{R}_i$ all have the same size and shape.

This model of an alloy can be solved exactly if the crystal is divided into supercells that contain $N$ atoms and are periodically reproduced to fill all space. The computer time required for a calculation of the electronic states for such a supercell normally increases as $N^3$, but sophisticated techniques for which the time increases as $N$ have been developed. An order-$N$ method that is particularly well adapted for calculations on transition-metal alloys is called the locally self-consistent multiple scattering method (LSMS).[11] In the LSMS calculations that have been done to date,[12] the one-electron potential is forced into the muffin-tin form and the supercell contains no more than 1024 atoms, restrictions that can be removed now that the computational technology has evolved. Neither of these restrictions affects the conclusions that will be quoted here, which have been independently confirmed by other order-$N$ calculations.[13]

The net charge associated with the site $i$ in the alloy is the difference between the integral of the electronic charge density $\rho(\mathbf{r})$ over the Wigner-Seitz cell $\Omega_i$ and the nuclear charge $Z_i$

$$q_i = \int_{\Omega_i} \rho(\mathbf{r}) d\mathbf{r} - Z_i \tag{1}$$

The order-$N$ calculations show that every $q_i$ is different, although the charges associated with $A$ atoms tend to be distributed around an average

$$q_A = \sum_{i \subset A}^{N_A} q_i, \tag{2}$$

and the $q_i$ on $B$ sites are distributed around

$$q_B = \sum_{i \subset B}^{N_B} q_i. \tag{3}$$

A model that reflects the correct distribution of charges in the alloy is called polymorphous. The KKR-CPA, along with other approximate theories for the electronic states in alloys, assumes an isomorphous model in which all of the $q_i$ associated with A sites are exactly equal to $q_A$, while all of those associated with $B$ sites are $q_B$.

The Madelung potential at site $i$ in the supercell is

$$V_i = \sum_{j \neq i}^{N} M(|r_i - r_j|) q_j. \tag{4}$$

where $M(|r_i - r_j|)$ is the Madelung matrix.[14] It has the effect of including the contributions from all the charges in the periodically reproduced supercells and approaches

$$M(|r_i - r_i|) \rightarrow \frac{1}{|r_i - r_i|}$$

as the size of the supercell approaches infinity. It has been pointed out that the only theoretically consistent choice for the Madelung potentials in an isomorphous model of an alloy is zero,[15] which means that the Coulomb energy

$$U_C = \sum_{i=1}^{N} q_i V_i \tag{5}$$

is zero in this model. Efforts have been made to include the Coulomb energy in an isomorphous CPA, but the difficulties are demonstrated by the fact that the critical parameter in the resulting CPA must be evaluated by order-$N$ calculations that are not part of the theory.[16]

In the KKR-CPA, the effective scattering matrix $\mathbf{t}_c$ is defined by the requirement that an $A$ atom or a $B$ atom embedded in a lattice with the effective scattering matrix on every other site gives no scattering on the average. A scattering path matrix sums all of the scattering events that take an electron from the central site, called 0, through all of the other sites and back to the central site. The scattering path matrix is $\tau_c^{A,00}$ when there is an $A$ atom on the central site and $\mathbf{t}_c$ on all the others. If there is a $B$ atom on the central site, it is called $\tau_c^{B,00}$. The equation that defines $\mathbf{t}_c$ is then

$$c_A \tau_c^{A,00} + c_B \tau_c^{B,00} = \tau_c^{00} \tag{6}$$

where $\tau_c^{00}$ is the scattering path matrix for a lattice with $\mathbf{t}_c$ on every site.

The PCPA is a single-site approximation in the same sense as all CPA's, but it builds in the fact that every $q_i$ is unique and the Madelung potentials are given by Eq. (4). In order to calculate the Madelung potentials correctly, it is necessary to use a supercell that is periodically reproduced to fill all space and the Madelung matrices. There is a different potential $\nu_i(\mathbf{r})$ for each of the $N$ sites in the supercell, which includes the Madelung potential, and a corresponding scattering matrix $\mathbf{t}_i$. The scattering path for a system with $\mathbf{t}_i$ on the central site and $\mathbf{t}_c$ on all other sites is $\tau_c^{i,00}$. The equation that defines the effective scattering matrix $\mathbf{t}_c$ in the PCPA is

$$\frac{1}{N} \sum_{i=1}^{N} \tau_c^{i,00} = \tau_c^{00}. \tag{7}$$

Conceptually, the PCPA is similar to an order-$N$ method known as the locally self-consistent Green's function method.[17]

The fact that the PCPA requires a supercell and a different self-consistent potential for each site makes the calculations more arduous than the KKR-CPA, but that is offset by the advantage that it treats the Coulomb effects as well as they can be within the single-site approximation. It might be thought that using a specific supercell for a PCPA calculation implies that the effective scattering matrix $\mathbf{t}_c$ is not unique. This question has been treated theoretically,[18] and the following calculations demonstrate numerically that the PCPA $\mathbf{t}_c$ is indeed unique.

## III. CALCULATIONS AND RESULTS

Metallic Cu, Pd, and Ag all have the face-centered cubic (fcc) structure, and all of their alloys have that Bravais lattice. The fcc lattice is made up of four interpenetrating simple cubic lattices, so a cubic supercell with four lattice constants on an edge contains 256 atoms. This is the supercell that is used for most of the PCPA calculations described here. The atoms are distributed on the sites of the fcc Bravais lattice with a random number generator, although other randomly controlled steps are required to achieve the desired concentrations. A fully relativistic version of the DFT-LDA is employed. There are two self-consistency steps in a CPA calculation, the equations for the one-electron potentials

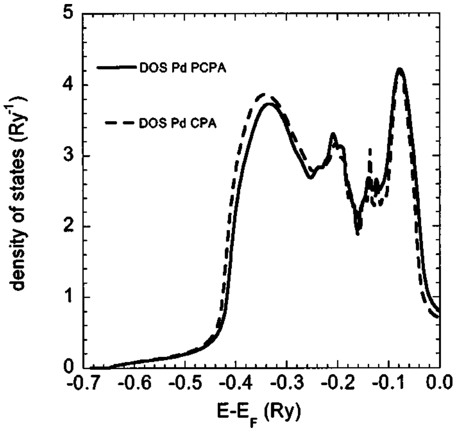

FIG. 1. The Pd density of states for $Cu_{0.75}Pd_{0.25}$ alloys calculated with the CPA and PCPA and plotted as a function of energy with respect to the Fermi energy. The DFT-LDA calculations are fully relativistic for both cases. The supercell used in the PCPA calculations has 256 Cu and Pd atoms randomly distributed on the lattice sites using a random number generator. The dotted line shows the KKR-CPA results and the continuous line shows the PCPA.

$\nu_i(\mathbf{r})$ are solved self-consistently as is Eq. (7) for the effective scattering matrix $\mathbf{t}_c$. The convergence of the calculations is rapid on a massively parallel supercomputer.

Figure 1 displays the Pd DOS in a $Cu_{0.75}Pd_{0.25}$ alloy calculated with the PCPA and the KKR-CPA. The difference is obvious and significant. We have calculated the DOS for $Cu_{0.05}Pd_{0.95}$, $Cu_{0.25}Pd_{0.75}$, $Cu_{0.40}Pd_{0.60}$, $Cu_{0.50}Pd_{0.50}$, $Cu_{0.75}Pd_{0.25}$, $Cu_{0.80}Pd_{0.20}$, and $Cu_{0.95}Pd_{0.05}$. From these calculations we observe that the difference between Pd DOS calculated with the KKR-CPA and the PCPA increases with increasing Cu concentration, so the difference between the two calculations for $Cu_{0.95}Pd_{0.05}$ is larger than that shown in Fig. 1. The Cu DOS calculated with the KKR-CPA and the PCPA is shown in Fig. 2. The difference is discernible in the calculations, but too small to be seen in an experiment.

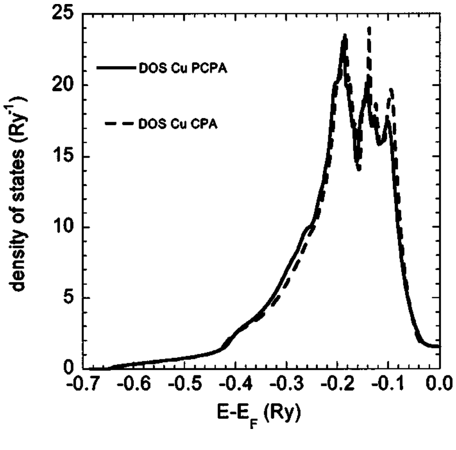

FIG. 2. The Cu density of states for $Cu_{0.75}Pd_{0.25}$ alloys calculated with the CPA and PCPA and plotted as a function of energy with respect to the Fermi energy. The DFT-LDA calculations are the same as in Fig. 1. The dotted line shows the KKR-CPA results and the continuous line shows the PCPA.

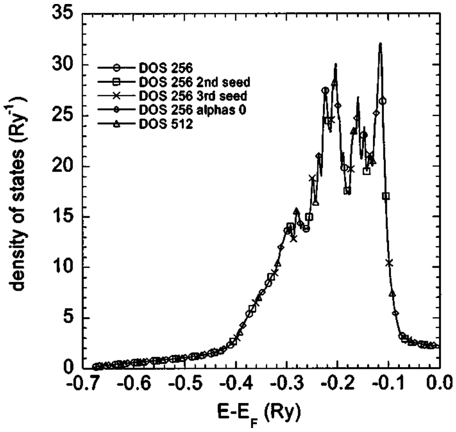

FIG. 3. The densities of states of a $Cu_{0.95}Pd_{0.05}$ alloy using the various PCPA calculations described in Sec. III.

Since the KKR-CPA applies to an infinitely large perfectly disordered lattice while PCPA calculations require an $N$ atom supercell, the latter calculations need to be tested for convergence in $N$. A test was made by increasing the size of the supercell from 256 to 512 atoms for a $Cu_{0.95}Pd_{0.05}$ alloy. The root mean square difference between the DOS obtained from the two calculations is 0.00533 on a scale that runs from 0.0 to 35.0 states per atom. Another concern is that the results of a PCPA calculation might not be unique because there are many random distributions of $A$ and $B$ atoms with a fixed concentration on 256 sites. Uniqueness was checked by repeating the PCPA calculations with three different seeds for the random number generator. Each seed leads to a completely different arrangement of the atoms in the supercell, although they are all random and have the same composition $Cu_{0.95}Pd_{0.05}$. The root mean square difference between the DOS obtained using the second and first seed is 0.049 while the difference between those using the first and third seed is 0.104.

The degree of disorder in a binary alloy is measured by the Warren-Cowley short-range order coefficients $\alpha(i)$ which should be zero for every nearest-neighbor shell $i$ in the ideally disordered structure. This cannot be achieved for a supercell with the atoms distributed randomly because, from probability theory, the $\alpha(i)$ should have a normal distribution about the mean 0 with a standard deviation $\sigma(i)=1/\sqrt{Nn_{NN}^i}$, where $n_{NN}^i$ is the number of atoms in the $i$th nearest-neighbor shell. It has been suggested that a better choice of the supercell would be to force the Warren-Cowley short-range order parameters for the first few nearest-neighbor shells to be zero.[16] This is an easy thing to do technically, and we calculated the DOS for a $Cu_{0.95}Pd_{0.05}$ alloy with the Warren-Cowley parameters for the first six shells set equal to zero. The root mean square difference between that DOS and the one for a random supercell is 0.0997, which is insignificant on a scale that ranges from 0.0 to 35.0.

The DOS from the different calculations for $Cu_{0.95}Pd_{0.05}$ alloys described in the two preceding paragraphs are all plotted in Fig. 3. As anticipated from the small values of the root mean square deviations, the lines all fall on top of one another. This is a graphic demonstration of the mathematical proofs in Ref. 18.

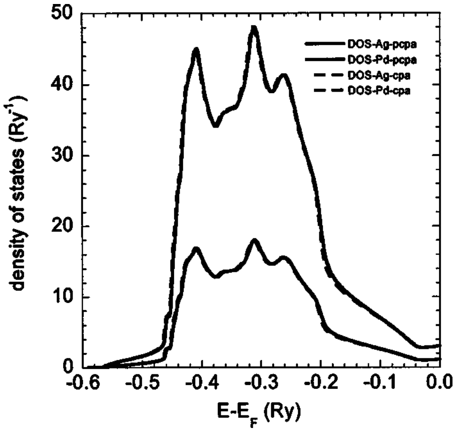

FIG. 4. The Ag and Pd partial densities of states of$Ag_{0.75}Pd_{0.25}$ alloy from CPA and PCPA calculations. The DFT-LDA calculations are fully relativistic for both cases. The supercell used in the PCPA calculations has 256 Ag and Pd atoms randomly distributed on the lattice sites using a random number generator. The KKR-CPA results are shown by the dotted line and the PCPA results with a solid line.

The Ag DOS and Pd DOS in $Ag_{0.05}Pd_{0.95}$, $Ag_{0.25}Pd_{0.75}$, $Ag_{0.40}Pd_{0.60}$, $Ag_{0.50}Pd_{0.50}$, $Ag_{0.75}Pd_{0.25}$, $Ag_{0.80}Pd_{0.20}$, and $Ag_{0.95}Pd_{0.05}$ were calculated. A typical example, $Ag_{0.25}Pd_{0.75}$, is shown in Fig. 4. It is clear that the corrections to the KKR-CPA theory obtained with the PCPA are unimportant for this case.

## IV. CONCLUSIONS

The PCPA calculations show that the Ag atoms in $Ag_{0.75}Pd_{0.25}$ have an average charge of −0.03168 electron charges ($e$), while the average charge on the Pd atoms is 0.09505$e$. This is a relatively small charge transfer, and the KKR-CPA calculations predict a charge of −0.02482$e$ on the Ag atoms and 0.074449$e$ on the Pd atoms, which is almost the same. Thus, the improvement in the treatment of the Coulomb energy with the PCPA is not important for Ag-Pd alloys, and that is the reason that the densities of states predicted by the two theories are identical.

The PCPA calculations show that the Cu atoms in $Cu_{0.75}Pd_{0.25}$ have an average charge of 0.0588$e$, while the average charge on the Pd atoms is −0.1764$e$, a sizable charge transfer. They give the same charge transfer as the first-principles LSMS calculations.[15] The KKR-CPA predicts 0.02505$e$ for Cu and −0.07514$e$ for Pd, a significant error. It is thus not surprising that the densities of states predicted by the two theories are different.

In Fig. 5 we reproduce the Pd partial spectral weight for $Cu_{0.75}Pd_{0.25}$ from XPS and UPS measurements using the data from Fig. 7 of Ref. 9. The authors used spectra at $h\nu = 40.8$ eV, where the Pd cross section is stronger, and those at $h\nu = 130.0$ eV, where the Cooper minimum of Pd occurs, to separate the Cu and Pd PSW's. They calculated a Pd DOS to compare with their experimental PSW using the KKR-CPA DOS from Ref. 2. They modified it by including the matrix-element and lifetime effects as well as instrumental broadening. The major assumption in their analysis is that the matrix-element effects in alloys are the same as those in pure metals.[19] Their modified Pd DOS is also shown in Fig. 5. It can be seen that, although the overall agreement is quite good, the experimental PSW is still smaller than the one they calculated in the lower-energy region.

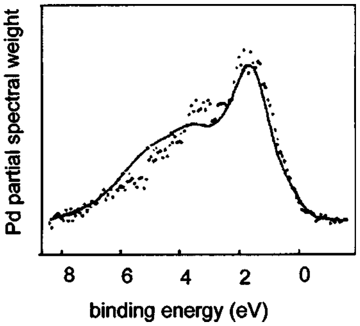

FIG. 5. Comparison of the Pd partial spectral weight (dots) with the calculated spectral weight for $Cu_{0.75}Pd_{0.25}$ using the KKR-CPA DOS from Ref. 2. Matrix-element effects and lifetime as well as instrumental broadening effects are included. The data and calculations are from Fig. 7 of Ref. 9.

The KKR-CPA DOS used in the calculations shown in Fig. 5 is the same as the one we calculate and show in Fig. 1. We cannot make the corrections used in Ref. 9 on our calculations because they require experimental data that is not available to us, but the effect of those corrections can be estimated because they simply scale the data. It can be seen from Fig. 1 that the Pd DOS obtained using the PCPA is reduced relative to the one obtained with the KKR-CPA in such a way that the agreement between the theory and results of the XPS and UPS measurements shown in Fig. 5 is significantly improved.

The observation that the inclusion of matrix-element, lifetime, and instrumental broadening effects makes it possible to explain the experimental PSW without invoking the effect of atomic displacements is a major conclusion of Refs. 9 and 19. The contribution of the present work is to show that the addition of Coulomb effects to the CPA calculations leads to even better agreement with experiment. The question of the magnitude of the atomic displacements in metallic alloys and their importance in explaining the properties of alloys is thus still open. There are few direct measurements of atomic displacements in concentrated alloys. An experimental study using extended x-ray absorption fine structure (EXAFS) measurements to study atomic displacements in Cu-Au alloys[20] is frequently quoted. The most reliable experimental measurements of atomic displacements are made with high-intensity high-resolution x rays from a synchrotron source. The best of these is a study of Fe-Ni alloys,[21] and it is impossible to judge the effects of magnetism on these data. Theoretical efforts to explain the Cu-Au data lead to contradictory conclusions.[22,23] Part of the difficulty is that all of the DFT-LDA calculations suffer from the fact that they predict a bond length for copper atoms in pure copper that is smaller than the experimental value. The generalized gradient approximation gives a better bond length for copper, but it predicts a bond length for gold in pure gold that is too large.[24] There is a need for more experimental and theoretical studies to resolve this tantalizing question.

## ACKNOWLEDGMENTS

This work was supported in part by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, and by the Laboratory Directed Research and Development program of Oak Ridge National Laboratory (ORNL), under Contract No. DE-AC05-00OR22725 with UT-Battelle. Much of the research was done during visits of the first author to the Metals and Ceramics Division at ORNL that were made possible by SURA Summer Cooperative Research Grants in Materials Science at ORNL that are administered by the Southeastern Universities Research Association (SURA). We thank Dr. Y. Wang for his valuable advice. Computations were performed on the Cray T3E at the National Energy Research Scientific Computing Center, the Cray T3E at the Pittsburgh Supercomputing Center, and on the Boca Cluster at the Florida Atlantic University.

---

[1] H. Winter, P. J. Durham, W. M. Temmerman, and G. M. Stocks, Phys. Rev. B **33**, 2370 (1986).

[2] B. Ginatempo, G. Y. Guo, W. M. Temmerman, J. B. Staunton, and P. J. Durham, Phys. Rev. B **42**, 2761 (1990).

[3] G. M. Stocks, R. W. Williams, and J. S. Faulkner, J. Phys. F: Met. Phys. **3**, 1688 (1973); H. Winter and G. M. Stocks, Phys. Rev. B **27**, 882 (1983).

[4] D. van der Marel, J. A. Jullianus, and G. A. Sawatzky, Phys. Rev. B **32**, 6331 (1985).

[5] 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).

[6] P. Weightman, H. Wright, S. D. Waddington, D. van der Marel, G. A. Sawatzky, G. P. Diakun, and D. Norman, Phys. Rev. B **36**, 9098 (1987); Y. Kucherenko, A. Y. Perlov, A. N. Yaresko, V. N. Antonov, and P. Weightman, *ibid.* **57**, 3844 (1998).

[7] R. S. Rao, A. Bansil, H. Asonen, and M. Pessa, Phys. Rev. B **29**, 1713 (1984).

[8] S. K. Bose, J. Kudrnovský, O. Jepsen, and O. K. Andersen, Phys. Rev. B **45**, 8272 (1992).

[9] T-U. Nahm, M. Han, S.-J. Oh, J.-H. Park, J. W. Allen, and S.-M. Chung, Phys. Rev. B **51**, 8140 (1995).

[10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn, *ibid.* **140**, A1133 (1965).

[11] Yang Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson, Z. Szotek, and W. M. Temmerman, Phys. Rev. Lett. **75**, 2867 (1995).

[12] J. S. Faulkner, Yang Wang, and G. M. Stocks, Phys. Rev. B **52**, 17 106 (1995); J. S. Faulkner, Yang Wang, and G. M. Stocks, *ibid.* **55**, 7492 (1997).

[13] I. A. Abrikosov, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, Phys. Rev. B **56**, 9319 (1997).

[14] M. P. Tosi, in *Solid State Physics*, edited by F. Seitz (Academic Press, New York, 1964), Vol. 16.

[15] B. Ujfalussy, J. S. Faulkner, N. Y. Moghadam, G. M. Stocks, and Yang Wang, Phys. Rev. B **61**, 12 005 (2000).

[16] A. V. Ruban and H. L. Skriver, Phys. Rev. B **66**, 024201 (2002).

[17] I. A. Abrikosov, A. M. N. Niklasson, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, Phys. Rev. Lett. **76**, 4203 (1996).

[18] J. S. Faulkner, Phys. Rev. B **64**, 233113 (2001).

[19] P. Weightman, R. J. Cole, C. Verdozzi, and P. J. Durham, Phys. Rev. Lett. **72**, 793 (1994); T-U. Nahm, Moonsup Han, S.-J. Oh, J.-H. Park, J. W. Allen, and S.-M. Chung, *ibid.* **72**, 794 (1994).

[20] A. I. Frenkel, E. A. Stern, A. Rubshtein, A. Voronel, and Yu. Rosenberg, J. Phys. IV **7**, C2-1005 (1997); A. I. Frenkel, V. Sh. Machavariani, A. Rubshtein, Yu. Rosenberg, A. Voronel, and E. A. Stern, Phys. Rev. B **62**, 9364 (2000).

[21] X. Jiang, G. E. Ice, C. J. Sparks, L. Robertson, and P. Zschack, Phys. Rev. B **54**, 3211 (1996).

[22] V. Ozolins, C. Wolverton, and A. Zunger, Phys. Rev. B **57**, 6427 (1998).

[23] A. V. Ruban, S. I. Simak, S. Shallcross, and H. L. Skriver, Phys. Rev. B **67**, 214302 (2003).

[24] A. Khein, D. J. Singh, and C. J. Umrigar, Phys. Rev. B **51**, 4105 (1995).