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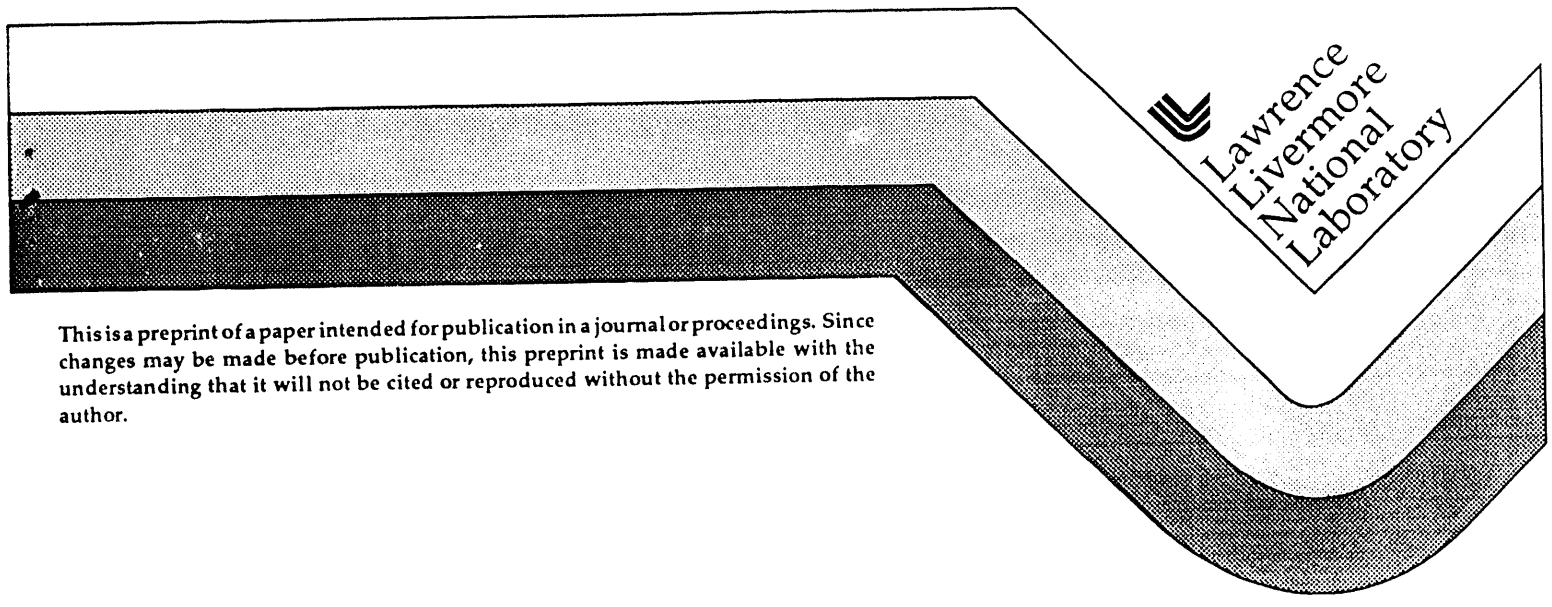

DISCLAIMER

CALCULATIONS OF NONSPHERICALLY AVERAGED CHARGE DENSITIES FOR SUBSTITUTIONALLY DISORDERED ALLOYS

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Abstract

Based on screening transformations of muffin-tin orbitals introduced by Andersen *et al.* [Phys. Rev. Lett. **53**, 2571 (1984)], we have developed a formalism for calculating the non-spherically averaged charge densities of substitutionally disordered alloys using the Korringa-Kohn-Rostoker coherent potential approximation (KKR CPA) method in the atomic-sphere approximation (ASA). We have validated our method by calculating charge densities for ordered structures, where we find that our approach yields charge densities that are essentially indistinguishable from the results of full-potential methods. For substitutionally disordered alloys, where full-potential methods have not been implemented so far, our approach can be used to calculate reliable non-spherically averaged charge densities from spherically symmetric one-electron potentials obtained from the KKR-ASA CPA. We report on our study of differences in charge density between ordered $AlLi$ in $L1_0$ phase and substitutionally disordered $Al_{0.5}Li_{0.5}$ on a face-centered cubic lattice.

Introduction

The use of energy-independent linear muffin-tin orbitals (LMTO's) as basis functions for solving the one-electron problem with a variational principle has led to the development of an accurate, reliable, and one of the most efficient approaches for describing the electronic structure of solids [1, 2]. In the LMTO formulation, the ease with which the structure-dependent part with no energy dependence separates out from the potential-dependent part facilitates application to simple as well as complex lattice structures. The energy linearization of the partial waves, the parametrization of the potential functions, and the construction of the potential in the atomic-sphere approximation (ASA) have all added to the efficiency of the LMTO method [3].

With the introduction of localized muffin-tin orbitals (MTO) [4, 5, 6, 7] in the LMTO method it has become possible to calculate the non-spherically averaged charge densities from the spherically symmetric one-electron potentials that compare very well with the computer-intensive full-potential results. Also, by evaluating the total energy functional without the ASA for the charge density we can make definitive statements about the stability of different ordered structures at $T = 0K$. Thus the approach described in Ref. [6], apart from providing a localized basis with its many uses [8], brings the LMTO-ASA method closer to its full-potential counterpart without adding any of the complexities inherent in the full-potential methods.

Some of the advantages offered by the conventional MTO's have been incorporated in the calculations of the electronic properties of substitutionally disordered alloys using the Korringa-Kohn-Rostoker coherent potential approximation (KKR CPA) method [9, 10, 11, 12]. As the KKR CPA with its spherically symmetric potential has been very successful in describing the electronic structure of substitutionally disordered alloys [13, 14, 15, 16], we would like to see if it can be improved further. An obvious and in many cases desirable improvement would require a full-potential implementation of the CPA. Since the full-potential CPA has not been implemented so far, although work in this direction is currently underway, any attempt at bringing KKR-ASA CPA results closer to the full-potential results should be welcomed.

In this paper we present a formulation of the KKR-ASA CPA based on the localized MTO's that allows us to calculate quantities such as non-spherically averaged charge densities as well as reproduces the results of Refs. [9, 10, 11] and [12] with an appropriate choice of representation. Our formulation starts out by setting up the Green functions using the generalized basis introduced in Refs. [4, 6]. Then by applying the process of ensemble-averaging as outlined in Ref. [13] we derive the ensemble-averaged Green functions appropriate for describing the electronic properties of substitutionally disordered alloys.

In the following we concentrate on that part of the Green function that contributes to the charge density, although our results can be easily extended to include terms that are left out. The two main references that we use throughout the paper are Ref. [6] and Ref. [13]. Here we closely follow the notation used in Ref. [17], where further details can be found as well.

General Formalism

As shown in Ref. [6] an appropriate energy-dependent muffin-tin orbital, which is continuously differentiable everywhere, can be written as

$$\chi^{\alpha}_{RL}(E,\mathbf{r}_R) = \phi^{\alpha}_{RL}(E,\mathbf{r}_R) + \sum_{R'L'} \dot{\phi}^{\alpha}_{R'L'}(E,\mathbf{r}_{R'}) h^{\alpha}_{R'L',RL}(E) + \chi^{\alpha,t}_{RL}(E,\mathbf{r}_R). \tag{1}$$

The muffin-tin orbitals, Eq. (1), reduce to the conventional MTO for $\alpha_{Rl} = 0$. When $\alpha_{Rl} \neq 0$, the MTO in that representation is obtained by noting that the potential functions $P^{\alpha}(E)$ and the structure constants S^{α} are related to the conventional potential functions $P^{0}(E)$ and the structure constants S^{0} through

$$P^{\alpha}(E) = P^{0}(E)/(1 - \alpha P^{0}(E)) \tag{2}$$

and

$$S^{\alpha} = S^{0}(1 - \alpha S^{0})^{-1}. \tag{3}$$

For $\alpha_{Rl} = \gamma_{Rl}$, the structure constants S^{γ} decay exponentially and they depend explicitly on the potential parameter γ_{Rl}. In the tight-binding representation, $\alpha_{Rl} = \beta_{Rl}$, the structure constants S^{β} become vanishingly small beyond the second nearest-neighbors for close-packed structures. The resulting MTO's are very localized and extend at most up to $2s$.

Now the part of the Green function that contributes to the charge density can be written as

$$G^{\alpha}(E,\mathbf{r},\mathbf{r}) = \sum_{R'L'}\sum_{RL} \chi^{\alpha}_{R'L'}(E,\mathbf{r}_{R'}) \left[\dot{P}^{\alpha}_{R'l'}(E)\right]^{(1/2)} \Sigma^{\alpha}_{R'L',RL}(E) \left[\dot{P}^{\alpha}_{Rl}(E)\right]^{(1/2)} \chi^{\alpha}_{RL}(E,\mathbf{r}_{R}) \,. \tag{4}$$

It is useful to rewrite the Green function, Eq. (4), in terms of on-site contribution, $G^{\alpha,on}_{RL',RL}(E,\mathbf{r},\mathbf{r})$, and off-site contribution, $G^{\alpha,off}_{R'L',RL}(E,\mathbf{r},\mathbf{r})$, because then the ensemble-averaging of the Green functions for the disordered alloys can be carried out in a simplified manner. From Eq. (4) the on-site and off-site contributions to the Green functions are seen to be

$$G^{\alpha,on}_{RL',RL}(E,\mathbf{r},\mathbf{r}) = \chi^{\alpha}_{RL'}(E,\mathbf{r}_{R}) \left[\dot{P}^{\alpha}_{Rl'}(E)\right]^{(1/2)} \Sigma^{\alpha}_{RL',RL}(E) \left[\dot{P}^{\alpha}_{Rl}(E)\right]^{(1/2)} \chi^{\alpha}_{RL}(E,\mathbf{r}_{R}) \tag{5}$$

and

$$G^{\alpha,off}_{R'L',RL}(E,\mathbf{r},\mathbf{r}) = \chi^{\alpha}_{R'L'}(E,\mathbf{r}_{R'}) \left[\dot{P}^{\alpha,A}_{R'l'}(E)\right]^{(1/2)} \Sigma^{\alpha}_{R'L',RL}(E) \left[\dot{P}^{\alpha}_{Rl}(E)\right]^{(1/2)} \chi^{\alpha}_{RL}(E,\mathbf{r}_{R}) \,, \tag{6}$$

respectively. Then the charge density, $\rho(\mathbf{r})$, can be evaluated by integrating the imaginary part of the Green function upto the Fermi energy, E_F.

$$\begin{aligned} \rho(\mathbf{r}) &= -\frac{1}{\pi} Im \int_{-\infty}^{E_F} G^{\alpha}(E,\mathbf{r},\mathbf{r}) \\ &= -\frac{1}{\pi} Im \int_{-\infty}^{E_F} \left[\sum_{RL'L} G^{\alpha,on}_{RL',RL}(E,\mathbf{r}_R,\mathbf{r}_R) + \sum_{R'L'}\sum_{RL} G^{\alpha,off}_{R'L',RL}(E,\mathbf{r}_R,\mathbf{r}_{R'}) \right] \end{aligned} \tag{7}$$

For describing the electronic structure of substitutionally disordered alloys made of atoms of type A and B, we associate with each lattice point a coherent potential function, $P^{\alpha,C}_{L}(E)$, determined self-consistently from

$$\begin{aligned} P^{\alpha,C}_{L}(E) &= C_A P^{\alpha,A}_{l}(E) + C_B P^{\alpha,B}_{l}(E) \\ &+ \left\{ P^{\alpha,A}_{l'}(E) - P^{\alpha,C}_{L'}(E) \right\} \Sigma^{\alpha}_{L'L} \left\{ P^{\alpha,B}_{l}(E) - P^{\alpha,C}_{L}(E) \right\} \,, \end{aligned} \tag{8}$$

where C_A and C_B are the concentrations of A and B atoms, respectively. The electronic properties of such alloys are calculated with the help of Green functions, which are the appropriate ensemble-averages of the on-site and off-site Green functions given by Eqs. (5) and (6), respectively. Within the KKR CPA formalism the process of taking the ensemble-average of on- and off-site Green functions is described in detail in Refs. [13, 14]. The multi-site nature of χ^{α} prevents us from directly applying the results of Ref. [13], but if we could make χ^{α} site-diagonal we should be able to carry out the ensemble-average of our Green functions using the procedure outlined in Ref. [13]. As we will show, the χ^{α}'s become site-diagonal in pure-L approximation. Thus, in the following we evaluate the ensemble-averaged Green functions within the pure-L approximation for χ^{α}'s.

The ensemble-average of the on-site (or off-site) Green function given by Eq. (5) (or 6) is taken by first averaging over all possible structures that leave the potential at the n-th site (or n- and m-th site) fixed, and then averaging over the possible occupations of

the n-th site (or n- and m-th sites) by atoms A and B. From Eq. (5) we see that the ensemble-averaged on-site Green function can be written as

$$\begin{aligned} G^{\alpha,C,on}_{RL',RL}(E,\mathbf{r},\mathbf{r}) &= C_A \chi^{\alpha,A}_{RL'}(\mathbf{r}_R)\left[\dot{P}^{\alpha,A}_{Rl'}(E)\right]^{(1/2)} D^{\alpha,A}_{RL',RL}(E)\Sigma^{\alpha}_{RL',RL}(E) \\ &\quad \left[\dot{P}^{\alpha,A}_{Rl}(E)\right]^{(1/2)} \chi^{\alpha,A}_{RL}(\mathbf{r}_R) \\ &+ C_B \chi^{\alpha,B}_{RL'}(\mathbf{r}_R)\left[\dot{P}^{\alpha,B}_{Rl'}(E)\right]^{(1/2)} D^{\alpha,B}_{RL',RL}(E)\Sigma^{\alpha}_{RL',RL}(E) \\ &\quad \left[\dot{P}^{\alpha,B}_{Rl}(E)\right]^{(1/2)} \chi^{\alpha,B}_{RL}(\mathbf{r}_R)\,, \end{aligned} \tag{9}$$

In Eq. (9) the superscript C stands for the ensemble- averaged Green functions.

Similarly, the ensemble-averaged off-site Green function is obtained by averaging over all structures that leave the potentials at sites n and m fixed, and then averaging over the possible occupations of sites n and m by atoms of type A and B. After ensemble-averaging, the off-site Green function, Eq. (6), becomes the ensemble-averaged off-site Green function becomes

$$\begin{aligned} G^{\alpha,C,off}_{R'L',RL}(E,\mathbf{r}_R,\mathbf{r}_{R'}) = & \{C_A \chi^{\alpha,A}_{R'L'}(\mathbf{r}_{R'})\left[\dot{P}^{\alpha,A}_{R'l'}(E)\right]^{(1/2)} D^{\alpha,A}_{R'L',R'L'}(E) \\ &+ C_B \chi^{\alpha,B}_{R'L'}(\mathbf{r}_{R'})\left[\dot{P}^{\alpha,B}_{R'l'}(E)\right]^{(1/2)} D^{\alpha,B}_{R'L',R'L'}(E)\} \\ &\left[\Sigma^{\alpha}_{R'L',RL}(E)\right] \\ &\{C_A \chi^{\alpha,A}_{RL}(\mathbf{r}_R)\left[\dot{P}^{\alpha,A}_{Rl}(E)\right]^{(1/2)} D^{\alpha,A}_{RL,RL}(E) \\ &+ C_B \chi^{\alpha,B}_{RL}(\mathbf{r}_R)\left[\dot{P}^{\alpha,B}_{Rl}(E)\right]^{(1/2)} D^{\alpha,B}_{RL,RL}(E)\}\,. \end{aligned} \tag{10}$$

Eqs. (9) and (10) represent the ensemble-averaged Green functions for the substitutionally disordered alloys in the coherent potential approximation. Within the approximations made so far and for $\alpha_{Rl} = 0$, the results for site-diagonal properties such as density of states calculated with the Green function given by Eq. (9) are identical to that of Ref. [9], as expected. The off-site Green functions are used to describe the non-site-diagonal properties of the substitutionally disordered alloys. Our main interest lies in the evaluation of the non-spherically averaged charge densities in the CPA, which can be calculated from

$$\rho^C(\mathbf{r}) = -\frac{1}{\pi} Im \int_{-\infty}^{E_F} \left[\sum_{RL'L} G^{\alpha,C,on}_{RL',RL}(E,\mathbf{r}_R,\mathbf{r}_R) + \sum_{R'L'} \sum_{RL} G^{\alpha,C,off}_{R'L',RL}(E,\mathbf{r}_R,\mathbf{r}_{R'}) \right]\,. \tag{11}$$

It can be easily shown that $\rho^C(\mathbf{r})$ can be written as the concentration-weighted average of the individual charge densities $\rho^A(\mathbf{r})$ and $\rho^B(\mathbf{r})$,

$$\rho^C(\mathbf{r}) = C_A \rho^A(\mathbf{r}) + C_B \rho^B(\mathbf{r})\,. \tag{12}$$

where $\rho^X(\mathbf{r})$ describes the charge density with X atom at the central site with $X = A$ or B. For a real-space evaluation of the charge density given by Eq. (11) we use the $\alpha_{Rl} = \beta_{Rl}$ representation and the pure-L approximation for the TB orbitals.

We have applied the formalism developed to the calculation of the non-spherically averaged charge densities of ordered AlLi in $L1_0$ phase and the substitutionally disordered $Al_{0.5}Li_{0.5}$ on a fcc lattice. For comparison with the charge densities of the substitutionally disordered $Al_{0.5}Li_{0.5}$, in Figs. 1(a) and 1(b) we show the charge densities of $L1_0$ AlLi in the (001) and (100) planes with Al and Li at the central site, respectively.

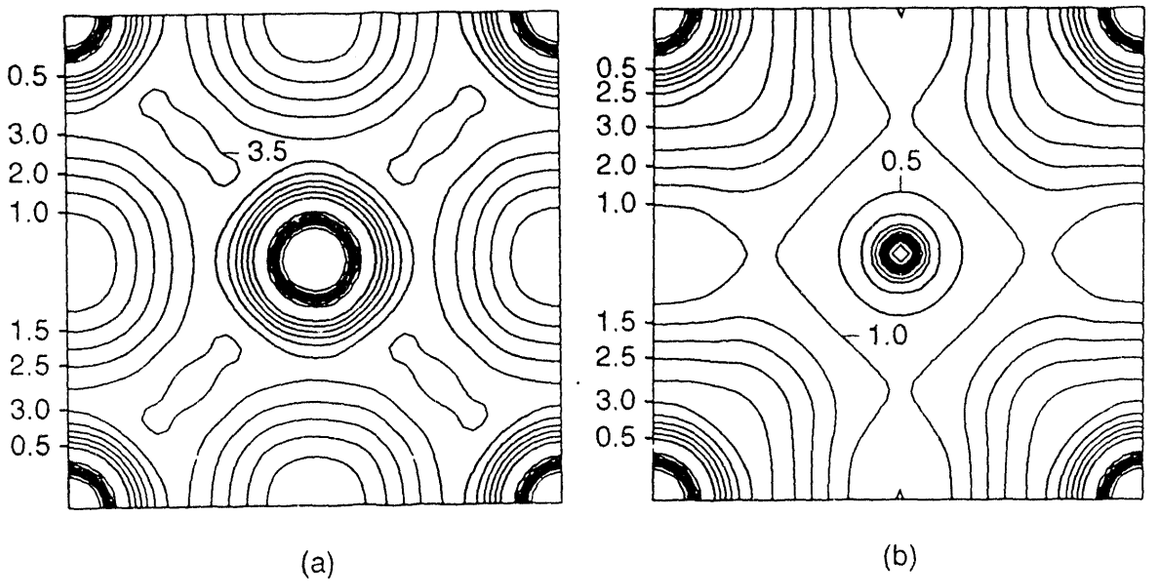

Fig. 1. The valence charge density of AlLi ($L1_0$) (a) in the (001) plane and (b) in the (100) plane calculated with the LMTO method and the pure-L approximation for the TB orbitals. The atom at the center in (a) ((b)) is Al (Li).

The differences in charge densities of $L1_0$ AlLi and the substitutionally disordered $Al_{0.5}Li_{0.5}$ in the (001) plane with Al at the central site are shown in Fig. 2(a). The most of the changes in charge density occur midway along the nearest-neighbors Al-Al directions. The decrease in charge density around the nearest-neighbor sites upon substitutional disordering, evident in Fig. 2(a), is due to the presence of CPA atoms at those sites. Some of the differences between the charge densities of ordered and substitutionally disordered alloys arise because of the change in the symmetries of the lattice involved. For example, the change in the charge densities due to change in symmetry in going from $L1_0$ for AlLi to fcc for $Al_{0.5}Li_{0.5}$ can be easily seen by comparing Fig. 1(b) with Fig. 2(b) which shows the charge density of the substitutionally disordered $Al_{0.5}Li_{0.5}$ in the (001) plane with Li at

the central site. As expected, the charge densities close to the individual atoms ($\approx 0.55w$) in disordered $Al_{0.5}Li_{0.5}$ remains essentially unchanged from the ordered AlLi system.

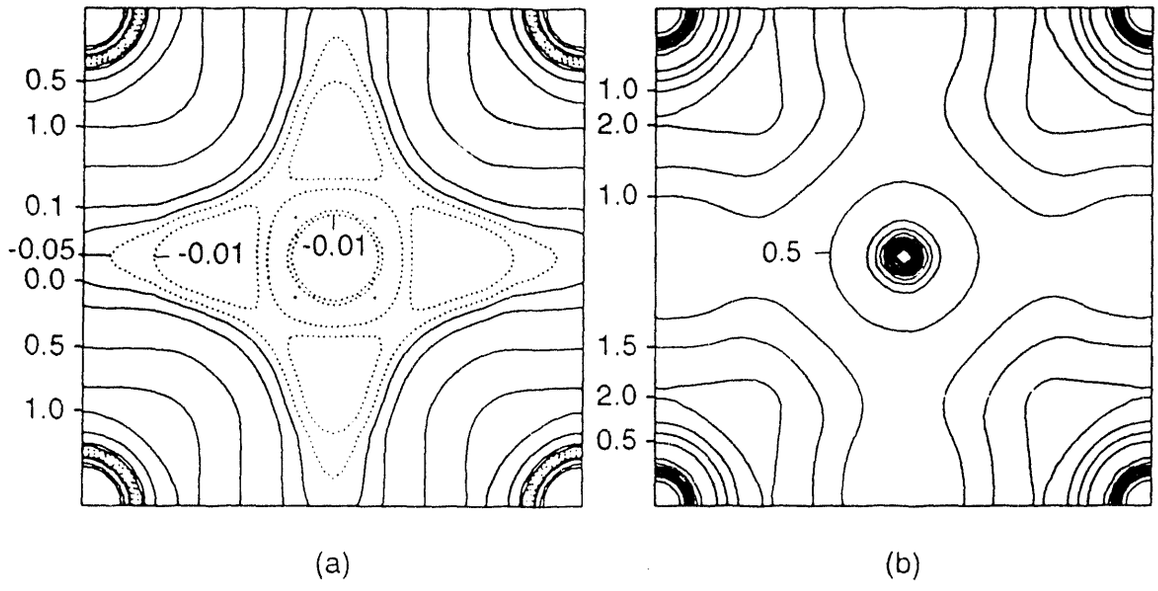

Fig. 2 (a) The differences in valence charge density between $L1_0$ AlLi and the substitutionally disordered $Al_{0.5}Li_{0.5}$ in the (001) plane of the fcc lattice. (b) The valence charge density of the substitutionally disordered $Al_{0.5}Li_{0.5}$ in the (001) plane of the fcc lattice. The atom at the central site in (a) ((b)) is Al (Li) while all other sites are occupied by CPA atoms. The contours are plotted at an interval of 0.5 in units of 10^{-2} electrons/(a.u.)^3.

We have presented a formulation of the KKR-ASA CPA that allows us to calculate electronic properties of substitutionally disordered alloys that are closer to their full-potential counterparts. We have demonstrated the usefulness of our approach by calculating the non-spherically averaged charge density for the substitutionally disordered $Al_{0.5}Li_{0.5}$ from the spherically symmetric one-electron potential obtained from the SCF KKR-ASA CPA method. Our approach also offers the possibility of more accurate total energy calculations as well as the inclusion of lattice relaxations in real-space for the substitutionally disordered alloys.

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