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Fully relativistic Korringa-Kohn-Rostoker coherent-potential-approximation embedded-cluster-method evaluation of short-range-order effects in substitutional alloys containing heavy elements

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We report calculations of densities of states associated with specific local atomic configurations in substitutionally disordered transition-metal-noble-metal alloys, in particular Au-Pd alloys. These calculations are based on the fully relativistic version of the Korringa-Kohn-Rostoker coherent-potential approximation and on the recently developed corresponding embedded-cluster method, and allow a direct evaluation of short-range-order effects in substitutionally disordered materials. A discussion of our results and a comparison with results obtained for transition-metal alloys such as Pd-Ag is given.

The introduction¹ of the coherent-potential approximation (CPA) provided a great advance in the study of substitutionally disordered alloys. In the CPA, the true disordered material is approximated by a periodic medium of effective scatterers, determined through the self-consistency condition that the scattering resulting when a real atom is embedded in the medium vanishes on the average. The CPA has a great number of desirable properties, and has been reviewed extensively in the literature.²⁻⁵ It has also been used successfully to calculate electronic densities of states^{3,6} (DOS's) and transport properties^{7,8} of disordered substitutional alloys.

As was realized almost simultaneously with its introduction, however, the single-site nature of the CPA precludes the treatment of statistical fluctuations away from the effective medium, and thus cannot be used in the study of short-range-order (SRO) effects in the electronic structure of disordered systems. Such statistical fluctuations may cause sharp structures in the DOS and can strongly influence physical properties, e.g., the formation of magnetic moments. Although a mean-field, linear-response theory⁹ can be used to obtain x-ray diffuse

scattering spectra in nonrandom binary alloys and thus provide direct information on the formation of stable ground states, it may be necessary to consider the nonlinear effects of local environment fluctuations in the study of phase stability and phase transformations in alloys. Consequently, many attempts at establishing a cluster or multisite generalization of the CPA have been reported.¹⁰⁻²²

Many of these attempts produced methods which were either too difficult to implement computationally, such as the molecular CPA,¹⁰ or failed to satisfy²² important analytic requirements. In other applications,²³ severe geometric simplifications such as the substitution of a Cayley-tree (or Bethe) lattice for the proper crystal structure of the material were made.

To date, the most successful approach to the study of SRO effects in substitutionally disordered alloys is afforded through applications of the embedded-cluster method (ECM).²⁴⁻²⁸ The ECM allows the exact treatment of a cluster of impurity atoms embedded in a translationally invariant effective medium, such as that determined in the single-site CPA. Although the ECM

is not a self-consistent cluster theory, it permits the calculation of the Green function (or the scattering matrix) associated with any given cluster configuration and thus can account directly for the effects of local statistical fluctuations. At the same time, however, the need remains for a fully satisfactory cluster theory in which the effects of SRO would be taken into account self-consistently.

The first applications of the ECM were made^{24,25} within a tight-binding (TB) description of the Hamiltonians for disordered alloys. More recently, the ECM has been applied^{26,27} to Hamiltonians of more realistic potential functions, e.g., those of a muffin-tin type, within the context of the Korringa-Kohn-Rostoker or Green-function formalism and in connection with the corresponding version of the CPA (KKR CPA). In most recent applications the ECM has been used^{29,30} in the calculation of effective multiatom interactions in substitutionally disordered transition-metal alloys.

In this paper we report a new implementation of the ECM which allows the proper treatment of a number of significant physical features such as relativistic effects, and eventually spin polarization, which figure prominently in the study of magnetic alloys and alloys containing heavy elements such as the actinides. This application of the ECM is based on the fully relativistic version (R) of the KKR CPA,³¹⁻³³ which already has been used in a number of calculations. The extension of the ECM to a fully relativistic treatment of disordered alloys presents a number of new features when compared to the nonrelativistic case, so that before presenting our results we give a brief exposition of some computational aspects of the formalism. In all our calculations we used potentials constructed using the Mattheiss prescription with Slater exchange. Such potentials seem to be consistent³⁴ with experimental data for the Au-N_{6,7} soft x-ray emission spectra in Au_x-Pd_{1-x}.

RELATIVISTIC KORRINGA-KOHN-ROSTOKER COHERENT-POTENTIAL APPROXIMATION AND THE EMBEDDED-CLUSTER METHOD

As has been discussed elsewhere,^{26,27} a computational implementation of the ECM requires the calculation of the site off-diagonal elements of the scattering matrix, or scattering path operator, associated with the RKKR-CPA effective medium. Formally these elements are given by the expression

$$\begin{aligned} \underline{\tau}^{ij} &\equiv \underline{\tau}(\mathbf{R}_j - \mathbf{R}_i) \\ &= \frac{1}{\Omega_{\text{BZ}}} \int \underline{\tau}(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} d^3k \\ &= \frac{1}{\Omega_{\text{BZ}}} \int [\underline{m}_c - \underline{G}(\mathbf{k})]^{-1} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} d^3k, \end{aligned} \quad (1)$$

where \mathbf{R}_i denotes a direct-lattice vector, Ω_{BZ} denotes the volume of the first Brillouin zone (BZ) of the reciprocal lattice, \underline{m}_c is the inverse of the single-site effective scattering matrix, \underline{t}_c , determined in the RKKR CPA, and $\underline{G}(\mathbf{k})$ denotes the familiar (relativistic) KKR structure constants at energy E and crystal momentum \mathbf{k} .

Rather extensive use of the group theory allows the restriction of the integral in Eq. (1) to the irreducible wedge, Ω_{IBZ} , of the BZ,

$$\underline{\tau}^{ij} = \sum_{R \in O_h} \frac{1}{\Omega_{\text{IBZ}}} \int \underline{D}^\dagger(R) \underline{\tau}(\mathbf{k}) \underline{D}(R) e^{i\mathbf{Rk} \cdot (\mathbf{R}_j - \mathbf{R}_i)} d^3k, \quad (2)$$

where $\{\underline{R}\}$ denotes the matrices of the Γ_{15} (t_{1u} -like) vector representation of the point group, and $\underline{D}(R)$ contains blockwise the Clebsch-Gordon coefficients which reduce the d^J -like representations. It should be noted that by using projective representations the summations in Eq. (2) can be restricted to a sum over the 48 operations of O_h rather than the 96 operations of the double group O_h^* . Furthermore, by making use of the properties of the inversion operator I , a left-coset decomposition can be employed, $O_h = \{O, IO\}$, so that we have

$$\begin{aligned} \underline{\tau}^{ij} &= \sum_{R \in O} \frac{1}{\Omega_{\text{IBZ}}} \int \underline{D}^\dagger(R) [\underline{\tau}(\mathbf{k}) [e^{i\mathbf{Rk} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \\ &\quad + e^{i\mathbf{Rk} \cdot (\mathbf{R}_i - \mathbf{R}_j)}] \underline{D}(R) d^3k, \end{aligned} \quad (3)$$

the summation including only 24 operations. It is clear that only $\underline{\tau}^{ij}$ corresponding to *different* distances $|\mathbf{R}_k - \mathbf{R}_l|$ need be calculated. For $|\mathbf{R}_i - \mathbf{R}_j| = |\mathbf{R}_k - \mathbf{R}_l|$ we obtain

$$\underline{\tau}^{kl} = \underline{D}^\dagger(R) \underline{\tau}^{ij} \underline{D}(R), \quad (4)$$

where $\underline{R}(\mathbf{R}_i - \mathbf{R}_j) = (\mathbf{R}_k - \mathbf{R}_l)$ with $R \in O_h$. For example, in a first-neighbor cluster in a fcc lattice one needs to calculate only five inequivalent $\underline{\tau}^{ij}$ (including trivially the site-diagonal element $\underline{\tau}^{00}$). All scattering path operators are calculated in the complex energy plane parallel to the real axis and deconvoluted to the real axis by means of a numerical Cauchy-Riemann continuation procedure for the calculation of the density of states. The BZ integrations for τ^{00} were performed using the 21 special directions of Fehner and Vosko,³⁵ whereas the five special directions of Bansil³⁶ were used in the calculation of the off-diagonal scattering path operators. In all cases a maximum number of 200 \mathbf{k} points were used along each direction.

It should be noted that care has to be taken when using (4) since in some cases, which can be denoted as "accidental" degeneracies, the group element R does not belong to O_h . However, R can always be identified with an element of the full rotation group. Such peculiar cases are shown in Table I of Ref. 37.

Finally, we mention that the use of the unitary properties of the symmetry operators

$$\exp[i\mathbf{Rk} \cdot (\mathbf{R}_i - \mathbf{R}_j)] = \exp[i\mathbf{k} \cdot \underline{R}^{-1}(\mathbf{R}_i - \mathbf{R}_j)]$$

allows one to employ familiar direction methods for evaluating the integral in Eq. (3).

Once the site off-diagonal elements $\underline{\tau}^{ij}$ have been determined, the local density of states associated with site i and cluster configuration J can be obtained from the expression

$$n_i^j(E) = -\frac{1}{\pi} \text{Im Tr} \underline{R}^\alpha [\underline{\tau}^j]_{ii}, \quad (5)$$

where site i is assumed to be occupied by an atom of type α . In this equation, the supermatrix $[\underline{\tau}^j]^{-1}$ is defined by its matrix elements,

$$\{[\underline{\tau}^j]^{-1}\}_{ij} = (\underline{m}^i - \underline{m}^c) \delta_{ij} + [\underline{\tau}^{-1}]_{ij}, \quad (6)$$

where \underline{m}^i is the (inverse) scattering matrix for the atom occupying site i , and $[\underline{\tau}]_{ij} \equiv \underline{\tau}^{ij}$ is the matrix of the intra-cluster effective-medium matrix elements given by Eq. (3). Finally, the matrix \underline{R}^α in Eq. (5) consists of the radial integrals

$$R_{QQ'}^\alpha = \int Z_Q^\alpha(\mathbf{r}, E) Z_{Q'}^\alpha(\mathbf{r}, E) d^3r, \quad (7)$$

with $Z_Q^\alpha(\mathbf{r}, E)$ being a properly normalized spinor.

APPLICATIONS TO Au₇₅Pd₂₅

Figure 1 depicts calculated density-of-states curves for the alloy Au₇₅Pd₂₅ obtained through the use of Eq. (5), where site i is chosen as the center of a nearest-neighbor cluster. Since Au₇₅Pd₂₅ shows a weakly split $d^{3/2}$ -like band, the various panels in the figure show $d^{3/2}$ -like (dashed curves) and $d^{5/2}$ -like (solid curves) partial DOS's for some extreme and some intermediate configurations of the 288 possible configurations, of the 12 nearest neighbors in the fcc lattice. In the left (right) side of the figure, the DOS's correspond to the center of the cluster being occupied by a Au (Pd) atom. (a) shows the species component DOS for a Au atom obtained in the RKKR CPA. The remaining panels depict the local density of states associated with a Au atom surrounded (b) by 12 Au atoms, (c) by 9 Au and 3 Pd atoms, and (d) by 12 Pd atoms. The right side of the figure shows the DOS obtained with Au and Pd center atoms interchanged.

As is seen in Fig. 1, the local environment does indeed affect the local DOS, the effect being a function of concentration. There is more change in the DOS of a Pd atom as the local environment is varied, than of a Au atom. The high Au concentration diminishes the effect of local fluctuations while greater changes may be expected when the environment around a Pd atom changes from all Au [Fig. 1(f)], to all Pd [Fig. 1(h)]. Overall, however, the changes due to SRO in this system are quantitatively smaller than in transitional alloys such as Pd-Ag.^{26,27} In the later case, the Pd d resonance lies above the Ag d band leading to the formation of a virtual bound state when small amounts of Pd are added to Ag. On the other hand, the Au and Pd $d^{3/2}$ and $d^{5/2}$ resonances are very close to one another and all lie inside both the Au and Pd d bands. As a consequence, the alloy is characterized by the presence of essentially a

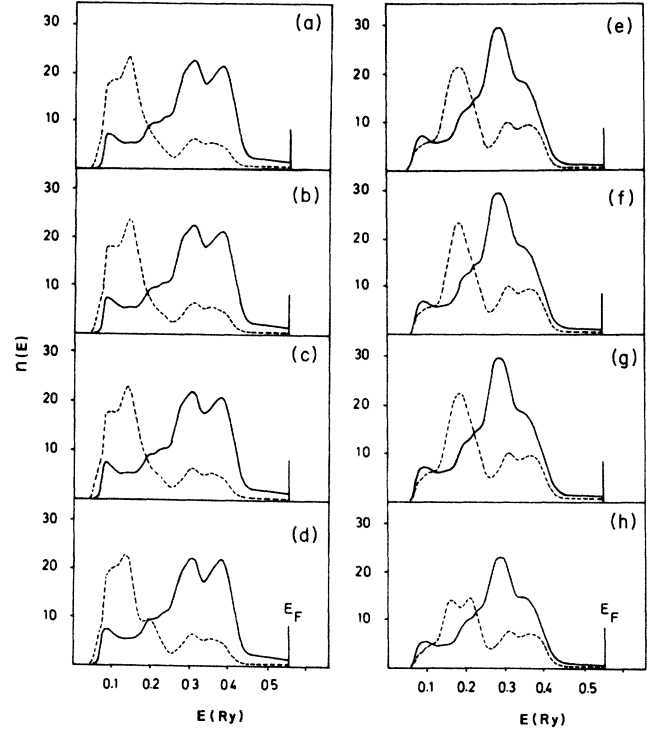


FIG. 1. $d^{3/2}$ -like (dashed curves) and $d^{5/2}$ -like (solid curves) DOS's for (a) an Au atom in the CPA, (b) an Au atom surrounded by 12 Au atoms, (c) by 9 Au and 3 Pd atoms, and (d) 12 Pd atoms. (e), (f), (g), and (h) correspond to (a), (b), (c), and (d) but with the Au atom at the center of the cluster replaced with a Pd atom.

common band, and SRO effects are, therefore, considerably smaller. In particular, at the Fermi energy of the CPA medium the DOS for the Au atom at the center of the cluster varies from 2.5495 (Pd-only neighbors), to 2.6488 (Au-only neighbors), with the CPA predicting 2.6479 states/Ry.

The results presented in this paper can be taken to be indicative of the flexibility of the method used to examine the effects of SRO in alloys in which relativistic effects can be expected to play a significant role. Since spin-only polarization can be taken into consideration rigorously,^{38,39} this method can be used to examine SRO effects in magnetic systems from a direct, first-principles point of view.

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