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Canonical description of electron states in random alloys

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The canonical method of Andersen and Jepsen for determining the band structure of metals, which is based on the linear muffin-tin orbital method and which leads to an extremely simple tight-binding method, is generalized to the case of random alloys. The factorization of the structural- and potential-dependent parts allows one to perform the configurational averaging within the single-site approximation. The theory is illustrated for the Ag_xPd_{100-x} alloy series.

The linear methods of band theory,[1] introduced a decade ago by Andersen, led to the development of very efficient computational schemes for the self-consistent determination of the band structure of solids. Among the linear methods, the linear muffin-tin orbital (LMTO) method[2] is the simplest and physically the most transparent one. Within the so-called atomic-sphere approximation (ASA) the LMTO method can be put into a form[3] combining the advantages of the tight-binding method and the Korringa-Kohn-Rostoker (KKR) method. We solve the standard eigenvalue problem with the tight-binding-like Hamiltonian, whose transfer matrix factorizes into the structure constant characterizing the geometry of the lattice and the potential parameters characterizing the potentials placed on the lattice sites. The theory provides us with reliable wave functions and offers a systematic description of variations in properties from metal to metal. It has been demonstrated recently[4] that the LMTO-ASA method can be successfully applied also to the study of isolated impurities in a perfect crystal. It is the purpose of this Rapid Communication to proceed further and to generalize the theory to the case of concentrated alloys within the single-site approximation[5] (SSA).

The starting point of our analysis is the tight-binding Hamiltonian in the orthogonal site representation, derived systematically from the LMTO-ASA theory and generalized to random alloys

$$\begin{aligned} H_{\mathbf{R}L,\mathbf{R}'L'} &= C_{\mathbf{R}l}\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'} \\ &\quad + \Delta_{\mathbf{R}l}^{1/2}\{\bar{S}[1-(Q-\bar{Q})\bar{S}]^{-1}\}_{\mathbf{R}L,\mathbf{R}'L'}\Delta_{\mathbf{R}'l'}^{1/2} \; . \end{aligned} \tag{1}$$

Here, $\mathbf{R}$ denotes the lattice site and $L=(l,m)$ is the orbital index (for transition metals $l \leq 2$). The quantities $X_{\mathbf{R}L,\mathbf{R}'L'} = X_{\mathbf{R}l}\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'}$, $X = C$, Q, and Δ are the conventional potential parameters[2] tabulated for all metals. The screened or tight-binding structure constant $\bar{S}$ contains all the information on the lattice geometry, and it is expressed in terms of the conventional structure constant[2,3] S and the screening parameter $\bar{Q}$ as[3]

$$\begin{aligned} \bar{S}_{\mathbf{R}L,\mathbf{R}'L'} &= [S(1-\bar{Q}S)^{-1}]_{\mathbf{R}L,\mathbf{R}'L'} \; , \\ \bar{Q}_{\mathbf{R}L,\mathbf{R}'L'} &= \bar{Q}_l\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'} \; . \end{aligned} \tag{2}$$

It has been shown by Andersen that fairly accurate (~ 10 mRy) band structures of metals are obtained with this Hamiltonian. The Hamiltonian (1) serves also as a bridge between the tight-binding and KKR methods: The transfer integrals are optimally parametrized through the potential parameters related to the phase shifts of potentials in atomic spheres.

The potential parameters $X_{\mathbf{R}l}$ take randomly the values X_l^A (X_l^B) with the probability x $(y=1-x)$ in binary alloys. The alloy electronic structure is fully described by the configurationally averaged resolvent $\langle G(z)\rangle$, where

$$\begin{aligned} G(z) &= (z-H)^{-1} \\ &= \{z-C-\Delta^{1/2}\bar{S}[1-(Q-\bar{Q})\bar{S}]^{-1}\Delta^{1/2}\}^{-1} \; . \end{aligned} \tag{3}$$

Here and below we often drop the indices $\mathbf{R}$ and L for simplicity. Because the Hamiltonian (1) exhibits both the diagonal and off-diagonal disorders, the configurational average of $G(z)$ cannot be performed within the SSA directly. To overcome this difficulty, we shall perform the transformation from the true resolvent $G(z)$ to the auxiliary one, $g(z)=[\bar{P}(z)-\bar{S}]^{-1}$. Here, the operator $\bar{P}(z)$ is diagonal in the site representation and it takes randomly the values

$$\bar{P}_l^Q(z) = (z-C_l^Q)/[\Delta_l^Q + (Q_l^Q - \bar{Q}_l)(z-C_l^Q)], \;\; Q = A,B \; . \tag{4}$$

The functions $\bar{P}_l(z)$ are easily recognized as so-called potential functions,[3] which are essentially the cotangents of the phase shifts parametrized into algebraic form (4). The true and the auxiliary resolvents have the same algebraic structure and are related by a simple scaling transformation[3,4,6]

$$\begin{aligned} G(z) &= \lambda(z) + \gamma(z)g(z)\gamma(z) \; , \\ \lambda(z) &= (Q-\bar{Q})\gamma(z)/\Delta^{1/2} \; , \\ \gamma(z) &= [d\bar{P}(z)/dz]^{1/2} \; . \end{aligned} \tag{5}$$

The screened structure constant $\bar{S}$ is a characteristic of a lattice,[3] and as such it is a nonrandom operator. Consequently, the auxiliary resolvent $g(z)$ exhibits only the site-diagonal disorder and the configurational average can be performed within the SSA exactly. For the configurationally averaged auxiliary resolvent $\langle g(z)\rangle$ we obtain[6]

$$\langle g(z)\rangle = [\mathcal{P}(z) - \bar{S}]^{-1} ,$$

$$\mathcal{P}_l(z) = x\bar{P}_l^A(z) + y\bar{P}_l^B(z) - \frac{xy[\bar{P}_l^A(z) - \bar{P}_l^B(z)]^2}{x\bar{P}_l^B(z) + y\bar{P}_l^A(z) - \Omega_{ll}(z)} , \tag{6}$$

$$\Omega_{ll}(z) = \mathcal{P}_l(z) - 1/\Phi_{ll}(z) ,$$

$$\Phi_{ll}(z) = \frac{1}{N}\sum_{\mathbf{k}} [\mathcal{P}(z) - \bar{S}(\mathbf{k})]_{ll}^{-1} .$$

The site-diagonal coherent potential function operator $\mathcal{P}(z)$ has for $l \leq 2$ and for cubic lattices four independent components $\mathcal{P}_l(z)$ ($l = s$, p, t_{2g}, and e_g) determined from the system of Eqs. (6) coupled via the diagonal elements of the configurationally averaged auxiliary resolvent $\Phi_{ll}(z)$ in the site representation. The central problem is how to express the true averaged resolvent $\langle G(z)\rangle$ in terms of the averaged auxiliary one $\langle g(z)\rangle$. The problem reduces to the averaging of expression (5) within the SSA. The first term in (5) is the site diagonal and it is averaged trivially. The second term represents the complicated average of three random quantities to which we shall apply the technique[7] proposed by us earlier. The result is[6]

$$\langle G(z)\rangle = \Lambda(z) + \Gamma(z)\langle g(z)\rangle\Gamma(z) ,$$

$$\Lambda(z) = \langle\lambda(z)\rangle + [\Delta\gamma(z)]^2 \frac{\langle\bar{P}(z)\rangle - \mathcal{P}(z)}{[\Delta\bar{P}(z)]^2} , \tag{7}$$

$$\Gamma(z) = \frac{\gamma^A(z)[\bar{P}^B(z) - \mathcal{P}(z)] - \gamma^B(z)[\bar{P}^A(z) - \mathcal{P}(z)]}{\Delta\bar{P}(z)} .$$

Here, the quantities $\Lambda(z)$ and $\Gamma(z)$ are site diagonal, $\langle X\rangle = xX^A + yX^B$ ($X = \lambda, \bar{P}$) and $\Delta X = X^A - X^B$ ($X = \gamma, \bar{P}$). Similarly to (5), the true averaged resolvent is obtained from the averaged auxiliary one by a scaling transformation.

Various physical quantities can be determined from the averaged one-particle Green's-function operator $\langle G(z)\rangle$. The simplest ones are the local density of states

$$\rho(E) = \pi^{-1}\,\mathrm{Im}\sum_l \langle G(E + i0^+)\rangle_{\mathbf{R}l,\mathbf{R}l} ,$$

and the Bloch spectral density

$$A(\mathbf{k},E) = -\pi^{-1}\,\mathrm{Im}\sum_l \langle G(\mathbf{k},E + i0^+)\rangle_{ll} .$$

Several remarks are merited: (i) An equivalent form of the theory is obtained for $\bar{Q} = 0$. The appropriate choice of $\bar{Q}$, however, guarantees an efficient screening of $\bar{S}$ leading to an important simplification of calculations.[3,6] (ii) For a crystal, our theory reduces naturally to the first-principles tight-binding method of Andersen and Jepsen.[3] In the low-concentration limit the problem is reduced[6] to the solution of the Dyson equation

$$g^{\mathrm{imp}}(z) = g^{(0)}(z) + g^{(0)}(z)\Delta\bar{P}(z)g^{\mathrm{imp}}(z)$$

describing a single impurity. The perturbation $\Delta\bar{P}(z) = \bar{P}^{\mathrm{imp}}(z) - \bar{P}^{(0)}(z)$ [the superscripts imp and (0) are related to the impurity and the host crystal, respectively] is limited to the impurity site due to the SSA character of our theory. The true perturbation $V = H^{\mathrm{imp}} - H^{(0)}$ extends, however, beyond the impurity site [see Eq. (1)]. The true impurity resolvent $G^{\mathrm{imp}}(z)$ is obtained from $g^{\mathrm{imp}}(z)$ using (5). This result can be considered as the simplest variant of the LMTO-ASA Green's-function method of Gunnarsson, Jepsen, and Andersen for a single impurity in a crystal.[4] (iii) A simpler, but meaningful variant of the theory is obtained by linearizing the potential function $\bar{P}(z)$ to the form $(z - \bar{C})/\bar{\Delta}$ appropriate, e.g., for narrow d bands.[6] The relation (5) then simplifies to

$$G(z) = (z - H)^{-1} = (\bar{\Delta})^{-1/2} g(z) (\bar{\Delta})^{-1/2} ,$$

with $\bar{H} = \bar{C} + (\bar{\Delta})^{1/2}\bar{S}(\bar{\Delta})^{1/2}$. The multiplicative form of this alloy Hamiltonian was anticipated, for example, by Harrison[8] and employed by us recently.[7]

We shall illustrate our theory on the evaluation of the densities of states and the spectral densities for the case of $\mathrm{Ag}_x\mathrm{Pd}_{100-x}$ alloys. We use tabulated potential parameters[2] for pure components. This choice is reasonable for closely packed metals with small charge transfer.[6,7] The results, given in Figs. 1 and 2, agree excellently with the self-consistent calculations using the KKR method.[9] The agreement between both types of calculations, though the present ones are non-self-consistent, indicates the importance of the proper positioning of constituent bands on the energy axis, which is natural in the ASA. On the other hand, the non-self-consistent implementation of the KKR method may suffer from the mismatch of the energy scales.[9] We note also very good quantitive agreement for some other alloy systems[6] for which the self-consistent KKR data are available (Cu-Pd alloys, spin-polarized Fe-Ni alloys, or hypothetical Fe-Ti alloy).

We shall briefly summarize the main features of our new method for calculation of the electronic properties of random alloys: (i) The present theory, based on the parametrization derived systematically from the LMTO theory, is a further development in the effort to establish

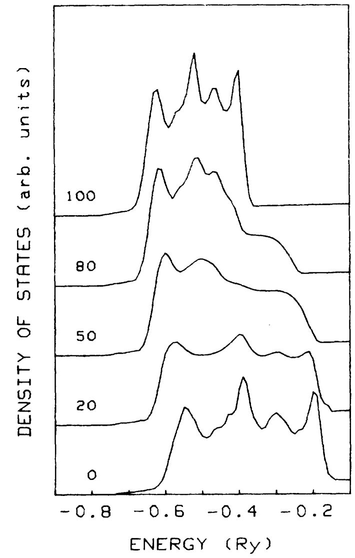

FIG. 1. Concentration dependences of the total densities of states of $\mathrm{Ag}_x\mathrm{Pd}_{100-x}$ alloys. Values of concentrations x are assigned to corresponding curves.

the quantitative tight-binding approach for alloys, whose main previous steps were the matrix generalization of the diagonal-randomness model[10] and the multiplicative-randomness model based on the universal parametrization scheme of Harrison.[7] (ii) The theory combines the simplicity of the tight-binding approach with the accuracy of the KKR method. We work with the tight-binding Hamiltonian whose parameters are derived systematically from the properties of potentials in atomic spheres. (iii) The generalization of the Andersen and Jepsen method to the SSA treatment of random alloys involves several nontrivial steps. We feel it necessary to mention them briefly though a detailed discussion cannot be given here and it is postponed to a further publication.[6] One group of problems concerns the use of crystal potential parameters for alloys: The transferrability depends on the choice of the size of atomic spheres and on the charge transfer between constituent atoms. These difficulties, present even in the case of ordered alloys, will be removed in the fully self-consistent version of the theory. Closely related is the problem of possible lattice relaxations and their influence on the alloy electronic structure.[11] Another problem that should be handled with care arises in connection with analytical properties of the resolvent operator in the complex energy plane. Seemingly, Eqs. (5) and (7) exhibit some unphysical poles that, of course, disappear in a proper treatment.

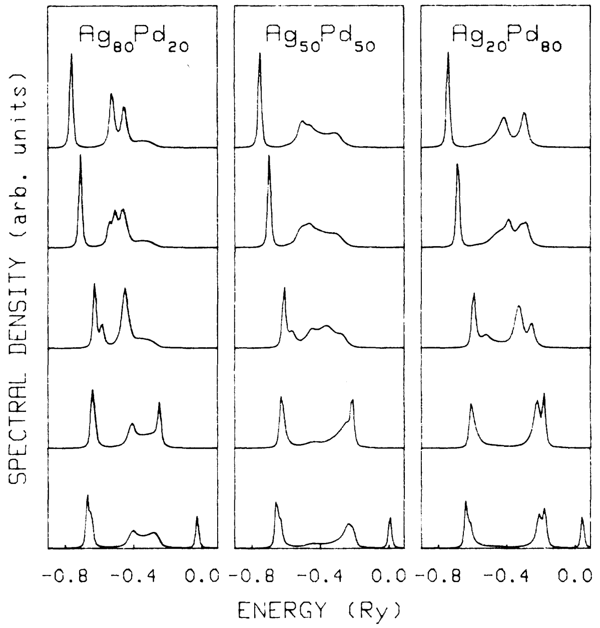

FIG. 2. Spectral density functions $A(\mathbf{k},E)$ for an equidistant set of $\mathbf{k}$ vectors along the Γ-X line (Γ-top curves, X-bottom curves) for the $Ag_{80}Pd_{20}$, $Ag_{50}Pd_{50}$, and $Ag_{20}Pd_{80}$ alloys.

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