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First-principles calculations of electronic structure in random hcp alloys: A Ru-Re example

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The electronic structure in random hcp transition-metal alloys is determined by means of the first-principles scalar-relativistic tight-binding linear muffin-tin orbitals method combined with the coherent-potential approximation. As an example, we have calculated electronic properties of the $\mathrm{Ru}_{1-x}\mathrm{Re}_x$ system which exhibits a non-rigid-band behavior and has the hcp structure in the whole concentration range.

Although the hexagonal-close-packed (hcp) structure is the most common one among the transition-metal alloys,[1] the bulk of the theoretical investigations in the past was restricted to cubic structures. The reason for it is a more complex structure of these materials due to two atoms per unit cell as well as the deviations from the ideal c/a lattice-constant ratio imposing certain structural anisotropies.

Regarding pure hcp metals, a number of band-structure calculations have been published (see, e.g., Ref. 2 and references therein). The results of the full-potential linear augmented-plane-wave (FLAPW) method[2] indicate that the non-muffin-tin terms in potential have a relatively small effect on the energy bands and the densities of states: in particular, the band structures obtained agree well with the linear muffin-tin orbitals (LMTO) calculations of Jepsen *et al.*[3] A comparison of the calculated electronic properties with available experimental data[2-6] indicates that the local-density approximation (LDA) provides their proper description.

The time thus seems to be ripe for a next step, namely, for a first-principles determination of the electronic structure of random hcp alloys. To our knowledge, no such calculations exist in the literature. It is the main purpose of the present paper to fill in this gap and to investigate the concentration dependence of the electronic properties of hcp random transition-metal alloys within the coherent-potential approximation (CPA).

We shall employ the recently developed CPA generalization[7] of the tight-binding linear muffin-tin orbitals (TB-LMTO) method,[8,9] which has been successfully used in a number of transition-metal alloys with one atom per unit cell, namely, in fcc and bcc random alloys.[10-13] Here we extend this approach to the case of two atoms per unit cell and apply it to the hcp transition-metal alloys.

Analogously as in Ref. 7, the starting point of our analysis is the Hamiltonian of an $A_{1-x}B_x$ alloy in the orthogonal LMTO representation given by

$$\begin{aligned} H_{\mathbf{R}L,\mathbf{R}'L'} &= C_{\mathbf{R}L}\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'} + \Delta^{1/2}_{\mathbf{R}L} S^{\gamma}_{\mathbf{R}L,\mathbf{R}'L'} \Delta^{1/2}_{\mathbf{R}'L'} , \\ S^{\gamma}_{\mathbf{R}L,\mathbf{R}'L'} &= [S^0(1-\gamma S^0)^{-1}]_{\mathbf{R}L,\mathbf{R}',L'} . \end{aligned} \tag{1}$$

Here $\mathbf{R}$ labels atomic positions and $L=(l,m), l \le 2$, is the orbital index. The quantities $X_{\mathbf{R}L}$, $X=C,\Delta,\gamma$, are the potential parameters[7-9] which describe the scattering properties of LDA potentials in atomic (Wigner-Seitz) spheres centered at $\mathbf{R}$. The potential parameters are closely related to the potential functions $P^0(z)$, which may be well approximated by the expression $P^0(z) = (z-C)/[\Delta+\gamma(z-C)]$. In the language of scattering theory, the functions $P^0(z)$ are proportional to cotangents of the corresponding phase shifts. In disordered alloys, the quantities $X_{\mathbf{R}L}$ take randomly two different values X^Q_L ($Q=A$ or B). The quantity $S^0_{\mathbf{R}L,\mathbf{R}'L'}$ represents the (analytically known[8,9]) canonical structure constant matrix characterizing the hcp lattice geometry independently of the occupation of the lattice sites by atoms. The S^{γ} is the structure constant matrix in the orthogonal representation.[8,9] In case of pure metals, the above Hamiltonian describes the electronic structure with an accuracy comparable to other first-principles methods.

In random alloys, the Hamiltonian (1) exhibits both diagonal and off-diagonal disorder, so that the CPA averaging of the resolvent $G(z)=(z-H)^{-1}$ cannot be done without additional approximations in the orthogonal LMTO representation. It was shown in Ref. 7 how to overcome this difficulty: we transform the resolvent from the orthogonal LMTO representation corresponding to the Hamiltonian (1) to a suitably chosen nonrandom LMTO representation α. This makes it possible to work with random, but site-diagonal potential function $P^{\alpha}(z)$ and with a nonrandom structure constant matrix S^{α} rather than with the Hamiltonian (1) also possessing the off-diagonal randomness. The usual CPA averaging procedure may be now applied to an auxiliary resolvent $g^{\alpha}(z)=[P^{\alpha}(z)-S^{\alpha}]^{-1}$ related uniquely to $G(z)$. In the last but nontrivial step[7] we transform the configurationally averaged resolvent $\langle g^{\alpha}(z)\rangle$ back to the original, orthogonal LMTO representation. The auxiliary LMTO representation α is conveniently chosen to be the most localized representation[7-9] $\alpha\equiv\beta$ with a nonrandom structure constant matrix

$$S^{\beta}=S^{0}(1-\beta S^{0})^{-1}\ , \tag{2}$$

where $\beta_{\mathbf{R}l}=(\beta_s,\beta_p,\beta_d)$ characterizes this representation.

The above procedure can also be applied to the hcp alloys. Here the following aspects are worth mentioning.

(i) In the hcp structure with two atoms per unit cell and with *s*, *p*, and *d*, orbitals at each site the problem has the dimension 18×18 instead of 9×9 common for lattices with one atom per unit cell. The structure constant matrix in the Bloch representation is expressed as[9]

$$S^{\beta}_{\mathbf{U}L,\mathbf{U}'L'}(\mathbf{k})=\sum_{\mathbf{T}}\exp(i\mathbf{k}\cdot\mathbf{T})S^{\beta}_{\mathbf{U}L,(\mathbf{U}'+\mathbf{T})L'}\ , \tag{3}$$

where $\mathbf{T}$ runs over all lattice translations and $\mathbf{U}$ and $\mathbf{U}'$ are the sites in the primitive cell. The screened structure constant matrix $S^{\beta}_{\mathbf{R}L,\mathbf{R}'L'}$ of the hcp lattice with a given c/a ratio was determined directly by performing the matrix inversion (2) for a cluster of 93 atoms. Test calculations have shown that using a 39-atom cluster for the determination of $S^{\beta}_{\mathbf{R}L,\mathbf{R}'L'}$ gives nearly identical results and even a 19-atom cluster yields also a reasonable description of the electronic structure. The resulting small spatial extent of S^{β} in the real space[9] allows us to perform the Bloch transform (3) by the direct summation, without Ewald procedure.

(ii) In cubic lattices and for $l\leq2$ the site-diagonal quantities are diagonal also with respect to the orbital index L. In the hcp structure, due to a lower symmetry, the site-diagonal quantities are nondiagonal with respect to the orbital index and, consequently, the solution of the CPA equations is more involved. The problem can be simplified for transition metals by solving the CPA equations for the *d* states only, while the broad *s* and *p* bands can be safely treated in the virtual-crystal approximation (VCA). In case of fcc and bcc transition-metal alloys we have found that this approximation causes only negligible deviations in comparison with the full treatment. In the hcp structure, the *d*-*d* block is diagonal with respect to the orbital index and there are three different values of matrix elements D_L: $D_{xy}=D_{x^2-y^2}$, $D_{yz}=D_{xz}$, and D_{3z^2-1}.

We have applied the above formalism (with the *s* and *p* states being treated within the VCA) to the substitutionally disordered hcp $\mathrm{Ru}_{1-x}\mathrm{Re}_x$ system, which exists in the whole concentration range and exhibits a non-rigid-band behavior so that a proper treatment of its electronic structure requires the use of the CPA. The experimental c/a ratios of Ru and Re are similar, being 1.583 and 1.615, respectively. For a random alloy $\mathrm{Ru}_{1-x}\mathrm{Re}_x$ we have used the value $(c/a)_{\mathrm{alloy}}=(1-x)(c/a)_{\mathrm{Ru}}+x(c/a)_{\mathrm{Re}}$. In the electronic structure calculations, the relativistic shifts were included, but the spin-orbit coupling was neglected. For the Brillouin-zone integration, we took 405 $\mathbf{k}$ points in an irreducible wedge. The integration method employed takes advantage of using the energy variable with a small imaginary part thereby smoothing out the integrand and speeding up the CPA iterations; the desired quantities as density of states (DOS) and spectral densities were found by the numerical analytical continuation back to the real energy axis[14] at the end of the CPA calculations. The energy resolution for energy-dependent quantities, e.g., the local DOS, was 0.01 Ry, and the CPA equations converged in all cases. As the input for the calculations, we used the potential parameters of pure Ru and Re, evaluated at their equilibrium lattice constants.[15] As discussed in detail in Ref. 11, the correctness of this choice is supported by two facts.

(i) Within the LMTO method, the potential parameters of different elements are related to a common energy zero, and the atomic spheres with radii equal to those of pure species remain approximately neutral also in a random alloy. This makes it possible to properly align the potential parameters on the energy scale and thus to achieve an approximate charge self-consistency. This is a great advantage in comparison with the Korringa-Kohn-Rostoker–CPA (KKR-CPA) method, where the misfit of constituents muffin-tin zeros and differently charged muffin-tin spheres prevent one from relating the phase shifts correctly on the energy scale, and either self-consistent calculations or empirical adjustments are inevitable.

(ii) The present choice of potential parameters implicitly assumes some sort of structural disorder due to different radii of atomic spheres, which leads to a trimodal (Ru-Ru, Ru-Re, and Re-Re) distribution of atomic distances, the Ru-Ru and Re-Re distances being essentially the same as in pure metals.[11] This picture of structural disorder is also supported by experiment.[16] In the tight-binding language, it means that the corresponding hoppings preserve their values from pure metals. Thus, the effect of lattice relaxations is also included in an approximate manner.[11] In the present case of Ru-Re alloys, this effect is rather small as the Wigner-Seitz radii of Ru and Re differ by only about 3%.

The band structure of Ru crystal along chosen high-symmetry directions in the irreducible hcp Brillouin zone is presented in Fig. 1. Overall band dispersion shapes agree well with those calculated by the augmented-plane-wave (APW) (Ref. 4) or FLAPW (Ref. 2) methods,

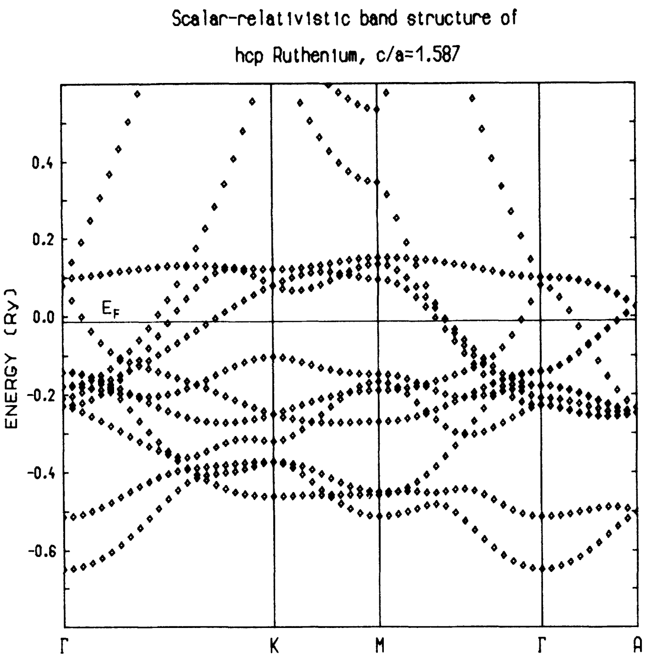

FIG. 1. Energy bands of hcp Ru along the high-symmetry directions in the Brillouin zone for the experimental c/a ratio.

by the pseudopotential approach,[6] and by the LMTO method.[3] The concentration dependences of the total DOS and of the local d DOS on Ru and Re atoms in a random $\mathrm{Ru}_{1-x}\mathrm{Re}_x$ alloy are shown in Fig. 2. The Ru-Re system exhibits a non-negligible off-diagonal disorder: $w_{\mathrm{Re}}/w_{\mathrm{Ru}}=1.35$ (w is the bandwidth). In contrast with the empirical TB-CPA approach, the present method allows to include it properly.[7] The d-level difference $\delta=C_d^{\mathrm{Re}}-C_d^{\mathrm{Ru}}=0.125$ Ry characterizing the diagonal disorder is rather large, but the ratio $\delta/\langle w\rangle$ $[\langle w\rangle=(1-x)w_{\mathrm{Ru}}+xw_{\mathrm{Re}}]$, which is a measure of the strength of disorder, is smaller than that found in strongly disordered fcc Ag-Pd or Cu-Ni random alloys. The Fermi level E_F of the alloys lies inside the d bands as Ru and Re are located in the middle of the transition-metal periods.

A characteristic feature of Ru and Re DOS are well-

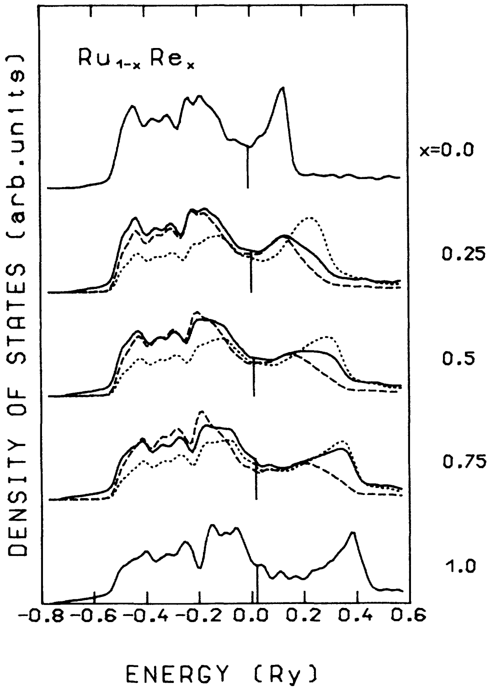

FIG. 2. The total (solid line) and the local densities of d states on the Ru atoms (dashed line) and on the Re atoms (dotted line) for $\mathrm{Ru}_{1-x}\mathrm{Re}_x$ random alloys. The concentrations x are assigned to the corresponding curves. The Fermi levels are indicated by vertical lines.

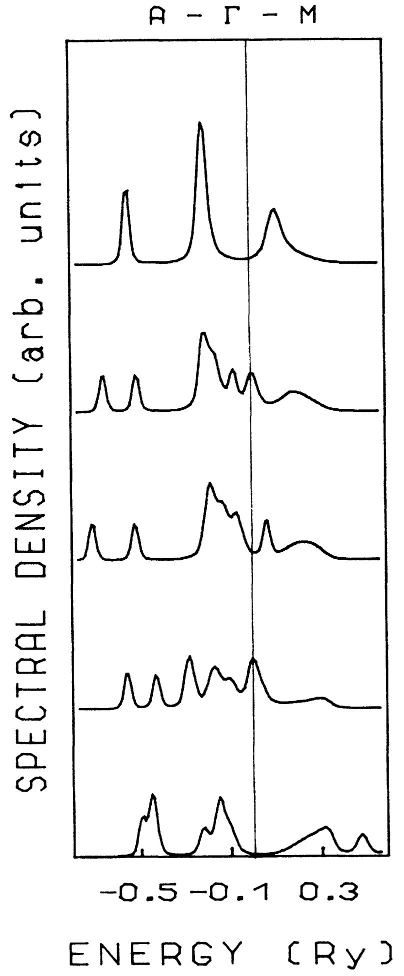

FIG. 3. The spectral density functions $A(\mathbf{k},E)$ for equally spaced $\mathbf{k}$ vectors along the $A-\Gamma-M$ line in the irreducible hcp Brillouin zone for $\mathrm{Ru}_{0.50}\mathrm{Re}_{0.50}$ random alloy. The top curve corresponds to point A, the middle curve to point Γ, and the bottom curve to point M. The position of the Fermi level E_F is indicated by the vertical line ($E_F=0.005$ Ry).

separated peaks above E_F, which differ in their widths and positions. Consequently, the unoccupied states above E_F in random alloys are influenced by disorder more significantly than occupied states below E_F, which is also reflected in the pronounced differences between the Ru and Re local densities of states for the states above the E_F. It will be interesting to test these conclusions in future on experiment using, e.g., the photoemission techniques applied to occuppied and empty (inversion photoemission) states. Note also an increase in the alloy bandwidth and a very slight increase in the Fermi level with increasing Re content.

The most detailed information on the electronic structure can be obtained from the Bloch spectral densities

$$A(\mathbf{k},E) \propto -(1/\pi)\mathrm{Im}\sum_{L} \langle \mathbf{k},L|\langle G(E+i0)\rangle|\mathbf{k},L\rangle ,$$

where $\langle G(E+i0)\rangle$ denotes the configurational averaging. The spectral density for $\mathrm{Ru}_{0.5}\mathrm{Re}_{0.5}$ random alloys is plotted in Fig. 3 along chosen high-symmetry directions in the hcp Brillouin zone. Significant deviations of the peak shapes from the Lorentzian form are clearly visible at energies above E_F. This again indicates that the effect of disorder is stronger above the E_F than below E_F, as already seen in the DOS.

We have presented the first *ab initio* calculations of the electronic properties of random hcp transition-metal alloys. Using the first-principles TB-LMTO-CPA method[7] extended to the case of two atoms per unit cell, it was possible to properly treat the electronic structure of nonrigid-band hcp alloys, which was illustrated on the $\mathrm{Ru}_{1-x}\mathrm{Re}_x$ system. The present approach may be improved by taking into account the spin-orbit coupling, which may be especially important for atoms from the 5*d* period.

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