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First-principles real-space linear-muffin-tin-orbital calculations of 3*d* impurities in Cu

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We have recently developed a scheme, based on the linear-muffin-tin-orbital (LMTO) formalism in the atomic-sphere approximation (ASA) and the recursion method, which allows us to perform first-principles, spin-polarized, density-functional electronic-structure calculations in real space. Here we use the real-space linear-muffin-tin-orbital (RS-LMTO-ASA) approach to study the behavior of 3*d* impurities (V,Cr,Mn,Fe) in a Cu host. We obtain the local density of states, the charge transfers, and local magnetic moments of the impurity and four adjacent shells of Cu atoms. Even though the procedures are quite different, our results for 3*d* impurities in Cu agree very well with those obtained using the well-established *ab initio* Korringa-Kohn-Sham Green's-function formalism. The RS-LMTO-ASA method does not require symmetry and can be used, with no extra effort, to study interstitial impurities and local disturbances in hosts with hcp or more complex structures. It can also be applied in the presence of lattice relaxation.

I. INTRODUCTION

A knowledge of the electronic structure is usually needed in order to understand the properties of metallic systems. For simple systems, the standard first-principles methods, implemented in reciprocal space, can be used to provide this information. But in the case of nonperiodic systems and systems with an extremely large number of atoms per cell, these methods are often inappropriate or inefficient. For these complex metallic systems, alternative ways of obtaining information about the electronic structure should be investigated. The recently developed first-principles real-space linear-muffin-tin-orbital (RS-LMTO-ASA) scheme[1] can often be helpful in this context.

The RS-LMTO-ASA scheme,[1] based on the LMTO-ASA formalism[2,3] and on the recursion method,[4] allows us to perform first-principles, spin-polarized, self-consistent, density-functional calculations directly in real space. The procedure is very similar to the regular **k**-space LMTO-ASA formalism,[2] but the solution of the eigenvalue problem is done in real space with the help of the recursion method.[4] The RS-LMTO-ASA scheme has been used with success[1,5] to obtain the electronic structure of nonmagnetic Zr_2Fe, ferromagnetic $FeNi_3$, and antiferromagnetic FeMn. In all cases, the results are in good agreement with those approached using the more traditional reciprocal-space approach.[1,5] The RS-LMTO-ASA scheme has also been applied to obtain the distribution of charge transfer in a large cell of 40 atoms, simulating amorphous Zr. Because in the RS-LMTO-ASA scheme the effort grows linearly with the number of inequivalent atoms, these calculations could be performed on a medium-sized machine (Digital Equipment Corporation VAX-6330 computer).[1] We should also note that, due to the use of the recursion method in the solution of the eigenvalue problem, the RS-LMTO-ASA codes can be easily implemented on parallel machines.

The problem of impurities is a classical problem, which has been understood in a qualitative way for a long time, within the context of empirical tight-binding model Hamiltonians. In the last few years there has been a renewed interest in the area, stimulated by new experimental techniques and more exact *ab initio* calculations. Recently, first-principles calculations of electric field gradients, isomer shifts, and hyperfine fields have also become available. These calculations can help with the interpretation of experimental data in these systems, and give information about the local environment around the perturbation.

There are several ways of treating local perturbations using a first-principles density-functional approach; one can use supercells in conjunction with the standard reciprocal-space methods, one can perform cluster calculations or use the Green's-function approach within some well-established formalism such as the Korringa-Kohn-Rostoker (KKR), LMTO, etc. The advantage of the Green's-function methods as compared to the other two approaches is that the embedding of the defect in the ideal crystal is described correctly.

In this paper we show that the RS-LMTO-ASA approach[1] can also be used to investigate local perturbations such as impurities, vacancies, etc., in metals. To illustrate the approach we obtain the local density of states, magnetic moments, and charge transfers for 3*d* impurities (V, Cr, Mn, and Fe) in a Cu host. The calculations for Fe have been previously reported.[6] The RS-LMTO-ASA approach allows us to work with very large clusters, of order of several thousands of atoms, avoiding the surface problems which make the embedding so crucial when using cluster methods. It uses a tight-binding Hamiltonian which allows for a more direct comparison with the model Hamiltonians frequently used to treat the impurity problem. Because the effort grows linearly with the number of atoms with inequivalent local density of states, the cost of treating *n* shells of atoms self-consistently is just $n+1$ times the effort of a single-site calculation. Again, the calculation can be performed on relatively small machines. The RS-LMTO-ASA scheme[1] does not require symmetry and is extremely flexible. It can be applied to interstitial impurities and is rather useful in the presence of lattice relaxation. The RS-LMTO-ASA scheme is also helpful when studying other kinds of local perturbations, such as defects and vacancies, and can be applied when the hosts have hcp and more complex structures. The scheme is also efficient in the study of local perturbations in metallic compounds with more than one type of atom in their cell, which are normally difficult to handle by other methods.

The paper is organized in the following way: in Sec. II, we briefly review the LMTO-ASA formalism in its several representations. In Sec. III, we describe the RS-LMTO-ASA scheme and discuss the modifications which have been introduced into the original scheme, in order to treat local perturbations. In Sec. IV, we give the results for 3*d* impurities in a Cu host. Finally, in Sec. V, we present our conclusions.

II. THE LMTO-ASA FORMALISM

In this section we give a brief description of the LMTO-ASA formalism to point out the approximations used and establish notation. The LMTO-ASA formalism is well known and has been described in several papers.[2,3,7,8] A review of the method and its several representations from a real-space point of view, with varying degrees of sophistication, can also be found in the literature.[1,9,10]

In the present work we use the atomic-sphere approximation (ASA), where the space is divided into Wigner-Seitz (WS) cells, which are then approximated by WS spheres of the same volume. We note that the LMTO is a linear method and the solutions are most accurate near a freely chosen energy E_ν. Here, as in most of the literature, E_ν is taken at the center of gravity of the occupied part of the given (*s*, *p*, or *d*) band. Finally, we should note that in the present paper we use a first-order Hamiltonian, where terms of order of $(E-E_\nu)^2$ and higher are neglected. As we shall see later, in this approximation the Hamiltonian has a simple tight-binding form, and the problem can easily be solved in real space.

The LMTO-ASA basis functions are chosen in order to optimize the efficiency when solving a given problem.[3] Normally, the information needed to set up the Hamiltonian can be divided into two independent parts. The first one depends only on the structure (the position of the atoms in space), while the second depends only on the solution of the Schrödinger equation at energy E_ν inside each inequivalent WS sphere, with appropriate boundary conditions. For the first part, the basic information is given by the canonical structure-constant matrix $S^0_{R'L',RL}$, which depends only on the structure, but not on the type of atoms occupying the sites.[3,7] The second part yields the so-called potential parameters for each site. The fundamental quantities in this case are the functions $\varphi_\nu(r)$, defined as the radial part of the solution of the Schrödinger equation for a spherical potential inside each WS sphere at energy E_ν, and its energy derivative $\dot{\varphi}_\nu(r)$ defined at energy E_ν.

Andersen and Jepsen[3] have shown that one of the characteristics of the LMTO-ASA formalism is that a variety of new basis sets can be constructed by taking appropriate mixing of the original standard LMTO basis functions. The mixing can be judiciously chosen to build into the problem some particularly desirable property. Because the sets are related through mixing, they can be obtained from each other. There are three very important LMTO-ASA representations. The first is the standard representation, in which the LMTO was originally formulated.[2] The second is the nearly orthogonal representation where the mixing parameters Q_l are chosen to make the overlap matrix close to unity.[8,9] Finally, we have the tight-binding (TB) or most localized representation, with a mixing chosen to make the interactions between neighboring sites as short ranged as possible.[3,7] In real space, it is convenient to work with a first-order Hamiltonian, where terms of order of $(E-E_\nu)^2$ and higher are neglected. To this order, the nearly orthogonal and TB representations coincide,[7] and we can take advantage of both features. Within this approximation, it is possible to work in the orthogonal representation, but express the orthogonal Hamiltonian in terms of localized parameters of the TB representation. Normally, the first-order approximation works quite well for metallic systems and one can always work with energy windows, if a higher precision is required.

In its present form, the first-principles RS-LMTO-ASA scheme is implemented within the approximations described above. Then the orthogonal Hamiltonian H, written in terms of TB parameters, has a very simple tight-binding form.[3,7]

$$H=\bar{C}+\bar{\Delta}^{1/2}\bar{S}\bar{\Delta}^{1/2} . \tag{1}$$

Here we follow the literature[7] and use quantities with bars ($\bar{S}$, $\bar{Q}_l$, $\bar{C}_l$, and $\bar{\Delta}_l$) to denote the most localized (TB) representation and quantities without bars (S, Q_l, C_l, and Δ_l) to denote the nearly orthogonal representation. The structure-constant matrix $\bar{S}$ for the TB representation, defined by a mixing $\bar{Q}_l$, is written in terms of the original canonical structure matrix S^0 as[7]

$$\bar{S}=S^0(I-\bar{Q}S^0)^{-1} . \tag{2}$$

Here I is the unit matrix and $\bar{Q}$ is a diagonal matrix with elements $\bar{Q}_l$. The mixing $\bar{Q}_l$'s which define the TB representation are found empirically,[3] by adjusting their value in expression (2), in order to obtain a localized structure constant matrix $\bar{S}$. The values of mixing were found to be approximately independent of the structure[3,8] and are given for *s*, *p*, and *d* electrons by $\bar{Q}_s=0.3485$, $\bar{Q}_p=0.053\,03$, and $\bar{Q}_d=0.010\,714$.

The mixing Q_l, and the other potential parameters C_l and Δ_l in the orthogonal representations, are given in terms of linear combinations of the solutions $\varphi_\nu(r)$ and $\dot{\varphi}_\nu(r)$, with appropriate logarithmic derivatives, substituted at the boundary of each WS sphere. These potential parameters have different values for every nonequivalent atom in the system. The potential parameters in the TB representation $\bar{C}_l$ and $\bar{\Delta}_l$, which appear in expression (1) for the Hamiltonian, can be obtained from the orthogonal parameters C_l, Δ_l, Q_l for a given E_ν by a simple expression:[7]

$$\frac{\bar{C}_l - E_{l\nu}}{C_l - E_{l\nu}} = \frac{\bar{\Delta}^{1/2}}{\Delta^{1/2}} = 1 - (Q_l - \bar{Q}_l)\frac{C_l - E_{l\nu}}{\Delta_l} \; . \tag{3}$$

In the orthogonal representation the overlap matrix is close to unity, giving rise to a simple eigenvalue problem of the form[7]

$$\begin{gathered} (H - E)u = 0 \; , \\ \psi_E = \sum_{R,L} \{\varphi_\nu(r_R) + (E - E_\nu)\dot{\varphi}_\nu(r_R)\} Y_L(\hat{\mathbf{r}}_R) u_{LR}(E) \; . \end{gathered} \tag{4}$$

In the first-principles RS-LMTO-ASA scheme[1] we use the recursion method[4] and the solutions of the Schrödinger equation within the WS spheres to find a self-consistent solution to this problem.

III. SELF-CONSISTENT RS-LMTO-ASA SCHEME FOR IMPURITIES

Here we briefly describe the recently developed RS-LMTO-ASA scheme, which allows us to perform first-principles, density-functional, electronic-structure calculations in real space. A more detailed description of the scheme can be found elsewhere.[1] We also discuss the modifications which had to be implemented in the RS-LMTO-ASA scheme in order to treat local perturbations.

The RS-LMTO-ASA self-consistent scheme is very similar to the regular LMTO-ASA **k**-space procedure, but when solving the eigenvalue problem to find the local density of states, we substitute the **k**-space diagonalization by a real-space recursion procedure.[4] As in reciprocal space, the problem of obtaining the Hamiltonian in RS can also be divided into two independent parts. The first part gives the structure-constant matrix $\bar{S}$ which connects each structurally inequivalent site to itself and to its close neighbors. These matrix elements are obtained by performing the matrix inversion of Eq. (2), on a small cluster of about 20 atoms around each site. The operation is done only once, because $\bar{S}$ does not depend on the potential and stays fixed during the self-consistent procedure. We note that because the inversion procedure does not require symmetry, it can be applied to interstitial sites and used in the presence of lattice relaxation and similar situations. The second part gives us the potential parameters, which change at each self-consistent step. To obtain $\bar{C}_l$, and $\bar{\Delta}_l$, we first determine the orthogonal potential parameters C_l, Δ_l, and Q_l. To get them we have to solve the Schrödinger equation inside each nonequivalent WS sphere. This part of the problem is often called "the atomic part" and is treated in the same manner as in the usual **k**-space formalism. Actually, we use the regular LMTO-ASA codes[11] when solving for the "atomic part" in the real-space approach. Because the atomic part gives all the nontrivial information about the potential, it is clear that the approximations for the exchange and correlation terms which we use in real space are exactly the same as those used in the regular **k**-space LMTO-ASA formalism. It can be shown[12] that the spherically averaged potential inside a WS sphere and the corresponding potential parameters are uniquely determined if some fundamental quantities are given. Those are the occupation $m^{(0)}$ for each local (s, p, and d) band at the site, the first moment (taken to be zero) and second moment $m^{(2)}$ of the local density of states relative to E_ν, and the logarithmic derivative of $\varphi_\nu(r)$ at the sphere boundary. Normally the logarithmic derivative D_l can diverge, and to avoid numerical problems, the related quantity P_l, which varies between zero and one, is often used:

$$P_l = 0.5 - \arctan(D_l)/\pi \; . \tag{5}$$

At this point it is useful to give a brief description of how the "atomic part" works. It can be shown (see Ref. 7) that the spherical average of the charge density inside a WS sphere can be expressed in terms of the solutions of the Schrödinger equation inside the WS sphere and the moments ($m^{(0)}, m^{(2)}$) of the local density of states (LDOS). To obtain the self-consistent charge density from given moments in practice, we start from a guessed charge density. The local density potential is constructed and $\varphi_\nu(r)$ and $\dot{\varphi}_\nu(r)$ are calculated to the given value of P_l. Then a new charge density is made by occupying the wave functions according to the given moments. This procedure is iterated, as indicated in Fig. 1, until the

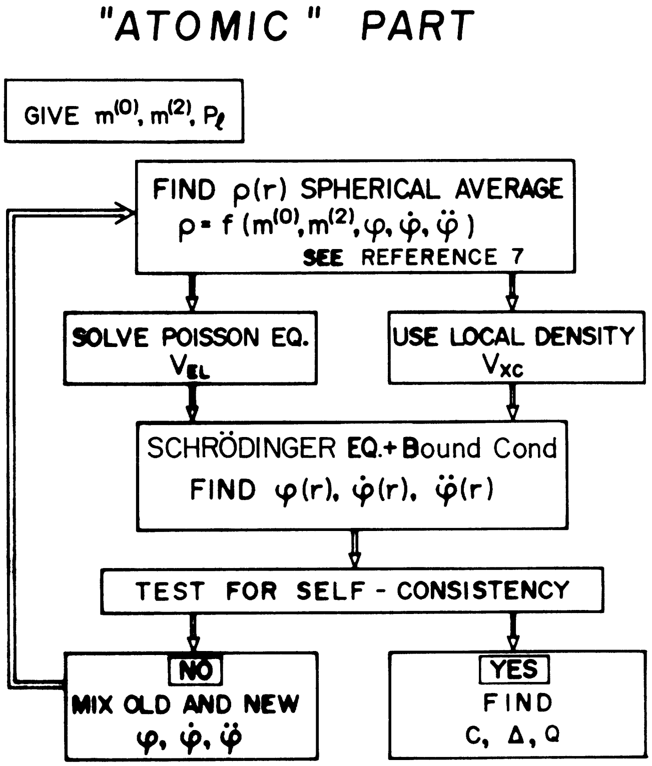

FIG. 1. Diagram of the "atomic" part, which gives the potential and radial solutions $\varphi(r)$, $\dot{\varphi}(r)$, and $\ddot{\varphi}(r)$ at E_ν. It generates the potential parameters C, Δ, and Q for given values of the moments and logarithmic derivatives at each WS sphere.

solutions inside the given WS sphere are self-consistent. We should note that when we solve for the "atomic part," we choose the potential to be zero at the sphere boundary. When constructing the Hamiltonian we should correct the relative energy scale of each WS sphere by its electrostatic potential (V_{es}). This correction includes the Madelung potential due to charged WS spheres of other sites at the given sphere and also takes into account the electrostatic contribution of the sphere itself. As we noted before, here the value of E_ν is chosen in order to always keep the first moment of the density of states for the occupied part of the band zero.

The RS-LMTO-ASA self-consistency process used here for the whole system is summarized in Fig. 2. We start by giving reasonable initial guesses for the occupation, second moment, and P_l for each of the nonequivalent WS spheres. Here, nonequivalent spheres are those with distinct densities of states. For example, all the 12 first neighbors of a substitutional impurity in a fcc host are considered equivalent, in this context. With these initial guesses, we use the "atomic part" of the codes, described above, to find the nearly orthogonal potential parameters and use Eq. (3) to obtain $\bar{C}_l$ and $\bar{\Delta}_l$. Finally we include V_{es} in the definition of $\bar{C}_l$ and build the real-space TB Hamiltonian of Eq. (1). To solve the eigenvalue problem and find the LDOS for s-p and d electrons at each nonequivalent site, we use the recursion method[4] on a large cluster (normally of at lest 1000 atoms), representing the system in question. We then use the LDOS to find the new energy E_ν and the new moments for each band at each nonequivalent site and the new values of P_l. We mix the old and new values of these quantities and apply them in the "atomic part" to get the new values of $\bar{C}$ and $\bar{\Delta}$, which will be used for the next iteration. The results will be converged when the moments and values of P_l obtained from the solution of the eigenvalue problem differ by less than a prescribed amount from the ones which generated the Hamiltonian. Because the step involving the recursion is the most expensive part of the procedure, it is often useful to implement rigid-band iterations between two recursion steps, to minimize charge fluctuations, and get better parameters for the next iteration.[1]

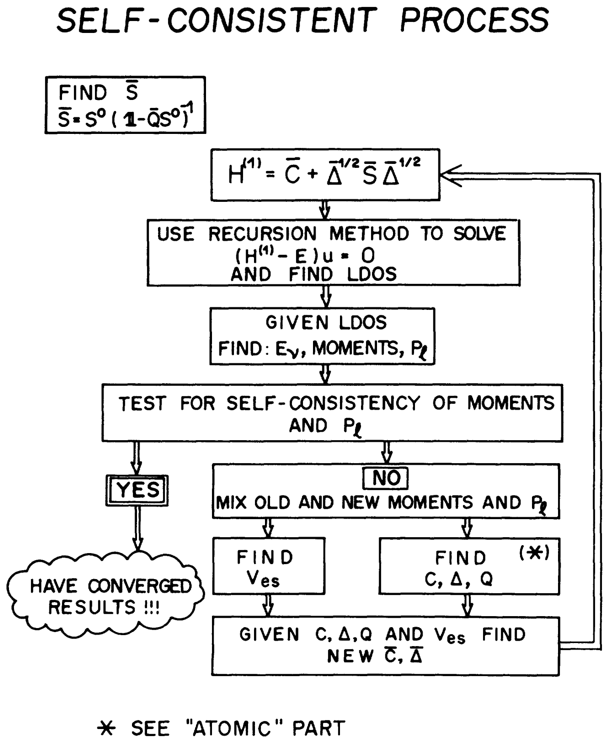

FIG. 2. Diagram showing the steps used to obtain self-consistent results within the RS-LMTO-ASA scheme used here. The "atomic" part, used to obtain the potential parameters C, Δ, and Q of the orthogonal representation is described in Fig. 1.

It is clear that to obtain the occupations and the moments of the LDOS, the Fermi level has to be determined. In a crystalline system, the Fermi level is determined at each self-consistent step, by filling the bands with the correct number of valence electrons. In the case of impurities and other local perturbations, the V_{es} contribution goes to zero far from the unperturbed region. In this case, the Fermi level of the perturbed system is fixed by the Fermi level of the host, and the procedure has to be modified to take that into account.

Here we describe the alternative procedure that we have developed in order to obtain the occupations and moments of the LDOS at each site, in the presence of local perturbations. First we perform a RS-LMTO-ASA calculation for the host and obtain the Fermi level, in the absence of perturbation, in the usual way. Then we set the Fermi level to this value and calculate the occupations and other relevant quantities in the presence of perturbation in the region of interest. Whatever extra charge results from the process inside the chosen region is placed on its immediate outer vicinity when determining the V_{es} at each inner site. The process is repeated until self-consistency is achieved.

In the case of the substitutional impurity considered here, we start the calculation by fixing the potential parameters at the Cu sites to their bulk values in pure Cu and giving an initial guess for the impurity parameters. Then we use the recursion method[4] to obtain the LDOS at the impurity site and obtain the occupation by filling the local band up to the Fermi level fixed by the pure host. If an extra charge is present at the impurity site, we assume that it has been transferred from the first shell of Cu atoms around the impurity. V_{es} at the impurity site is then obtained for this configuration of charges. The new potential parameters at the impurity site are then obtained by considering moments of the LDOS up to the fixed Fermi level. The new Hamiltonian is constructed and a new LDOS determined. The process continues until the impurity-site values are converged, with the Cu parameters fixed at the bulk values. Then we include the first shell of Cu atoms around the impurity in the self-consistent process. We find the LDOS for the impurity and its first Cu neighbor and obtain the occupation at the impurity and Cu sites by filling the bands up to the fixed Fermi level. Again, any extra charge is assumed to have originated in the first layer external to the region, here the second shell of Cu atoms. V_{es} at the impurity and first Cu neighbor is then obtained for this charge configuration. A new Hamiltonian is obtained and we proceed until the values for the impurity and its first Cu neighbors are all converged. We then include the second shell of Cu neighbors and the process is continued until the potential parameters for the last relaxed shell are the same, within our convergence requirements, as the bulk parameters. At this point, the charge transferred to the atoms outside the considered region should be negligible and all values calculated for the whole system will have reached convergence.

IV. RESULTS FOR 3*d* IMPURITIES IN A CU HOST

Here we present results for V, Cr, Mn, and Fe substitutional impurities in fcc Cu. The impurity and four shells of Cu neighbors are considered. The results for Fe, which have been previously presented,[6] were hard to obtain because a small mixing is required and a large number of recursion steps had to be performed. Here, we kept the same small mixing, but a rigid-band self-consistency was introduced between the recursion steps, reducing the number of recursion steps by a factor of 10. The slight differences in the results for the Fe impurity relative to the previous results[6] are due to better convergence in the present work.

Here we use the RS-LMTO-ASA scheme to obtain the LDOS, local magnetic moments, and charge transfers at the impurity site and four shells of Cu neighbors. To avoid surface effects we have used a large cluster of 1248 atoms, cut in order to keep the atoms of interest at a maximum distance from the surface. For all sites and all orbitals a cutoff parameters $L_{\max}=20$ was taken in the recursion chain and the Beer-Pettifor terminator[13] was used. We note that the recursion method gives only the general shape of the density of states. The detailed features can depend on the terminator used. But it is well known that the recursion method gives a very good description of integrated quantities and properties which depend on them. Therefore, the real-space scheme gives a qualitative description of the LDOS and of the density of states at the Fermi level, but is very reliable in obtaining magnetic moments, electric field gradients at the nuclei, and other properties which depend on integrated quantities. We note that the occupations and moments used in the RS-LMTO-ASA scheme are also integrals of LDOS, and therefore are very well described within the recursion method.

In the present calculation, to achieve convergence we have used a very small mixing (0.04 of the new moments and P_l and 0.96 of the old ones) at each iteration. An exchange correlation term of the form proposed by von Barth and Hedin[14] was used. From the process described in Fig. 1, it is clear that the moments and P_l can be used to determine the potential inside the WS spheres. Here, as it is often done in the regular reciprocal-space formalism, we use differences between the moments and logarithmic derivatives of subsequent steps to establish our convergence criteria. In practice, we start with an initial guess for the moments and logarithmic derivatives at the impurity site. After a few iterations, the initial charge oscillations are under control and we can start the rigid-band steps. We perform ten rigid-band iteration steps in between each recursion step (in the rigid-band iteration, the shape of each *s*, *p*, and *d* band is maintained, but the center of these bands are shifted to the new values of $\bar{C}_l$ at each step). The introduction of these steps considerably accelerates the approach to convergence.

Our convergence criteria for these calculations require that the moments and P_l obtained after a recursion step (with no mixing) not differ from the ones used to obtain the Hamiltonian by more than 0.001. We have noticed that the occupations, especially the *d*-electron occupations, are the last ones to converge. Here these occupations were converged up to 1 millielectron. We note that the errors introduced by the cutoff parameter $L_{\max}$ at a given step can be of the order of several millielectrons. But as we will see later, due to the action of screening, the error in a self-consistent calculation is very much reduced, being consistent with the convergence criteria adopted here.

In Fig. 3(a) we show our results for the LDOS at the impurity site in V, Cr, Mn, and Fe. For comparison, in Fig. 3(b) we shown results for the same quantities, obtained from KKR Green's-function (KKR-GF) calculations.[15] As we have mentioned before, the recursion method gives only the general shape of the LDOS. Even so, the agreement between the two approaches is, in all cases, extremely good. There are some differences in the LDOS above the Fermi level. We work within a first-order approximation to the Hamiltonian and E_ν is chosen at the center of the occupied band in order to give a good description of the occupied part of the band. Therefore, the empty states may be poorly described.

In Table I, we show our converged results for the magnetic moment at the impurity site (M_0) and the first four shells of the host (M_1, M_2, M_3, and M_4). For comparison we also show these same quantities obtained using the KKR-GF method converged with six shells of host neighbors.[16] Results for charge transfer for six converged shells are not given, but we could find KKR-GF results for charge transfers when only the impurity and one shell of neighbors were treated self-consistently.[15] In the last two rows of Table I, we also compare the charge transfers at the impurity site (C_0) and at the first Cu neighbor (C_1), obtained using the RS-LMTO-ASA and the KKR-GF approaches. In both cases only the impurity and the first shell of neighbors were converged. In Table II, we show our RS-LMTO-ASA results for charge transfers for the impurity (C_0) and four shells of neighbors (C_1, C_2, C_3, and C_4). The results for C_0 and C_1 are very similar to those of Table I, where only first neighbors were converged. We should note that the RS-LMTO-ASA and the KKR-GF procedures are quite different and the approximations used are not the same. For example, the density of states for empty states is often used in the KKR-GF approach when obtaining the real part of the Green's function for the host. In our scheme, the empty states are never used. Therefore, the agreement between the approaches is rather impressive, especially when we consider the small values of the induced moment at the Cu shells. In our opinion the different approximations used could justify larger differences than the ones observed here, when very small quantities are considered.

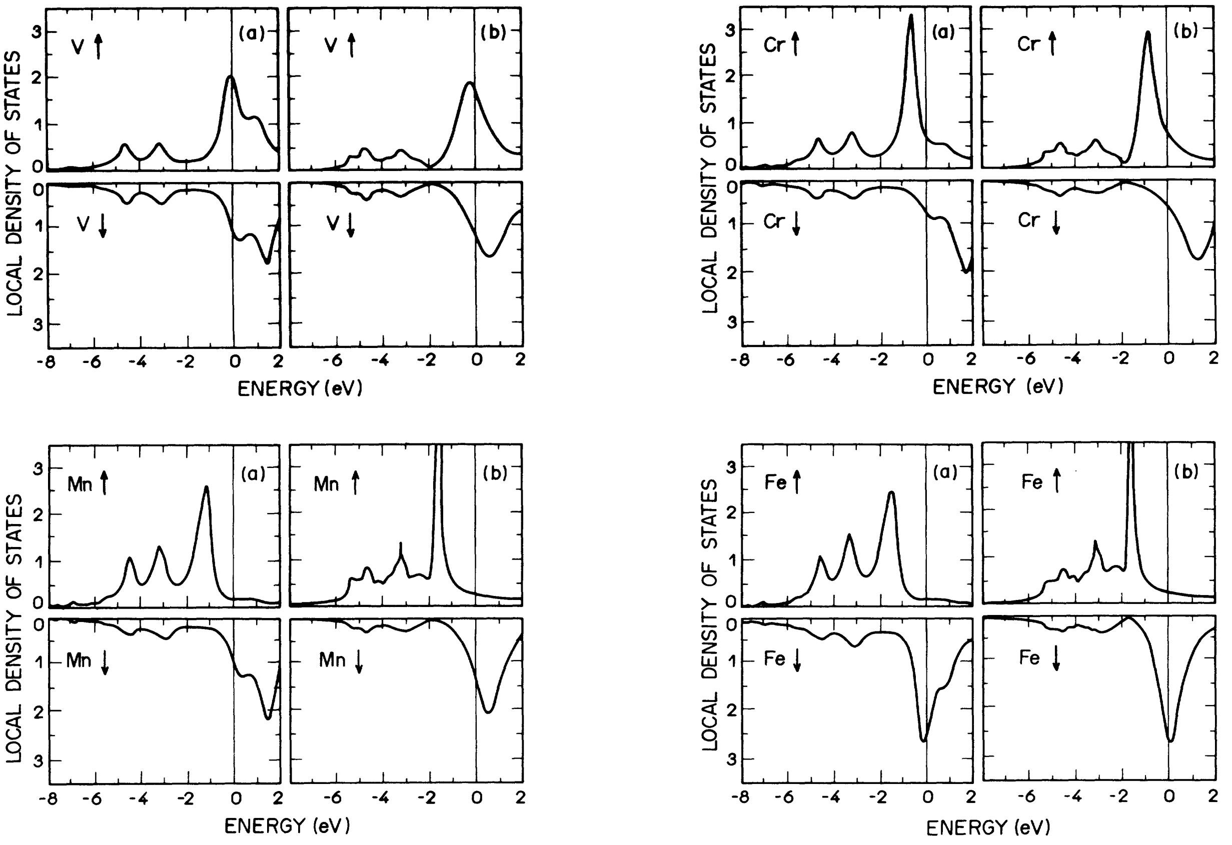

FIG. 3. Local density of states for up (↑) and down (↓) spins at the impurity site for V, Cr, Mn, and Fe impurities in a fcc Cu matrix. In (a) we show results from the RS-LMTO-ASA calculations performed here. In (b), for comparison, we show KKR-GF results for the same systems. The LDOS is given in units of states/eV atom spin.

This may eventually happen in other systems.

There are in the literature KKR-GF results for the magnetic moment of 3*d* impurities in Cu, obtained using a varied degree of accuracy; the single-site (SS) results,[17] where the impurity is converged while the Cu atoms maintain their bulk characteristics; results including the impurity and first shell of neighbors in the convergence;[15] and finally the latest ones, where six shells of neighbors were included.[16] It is interesting to compare the changes in magnetic moment (and charge transfers) obtained by the KKR-GF method and by our approach, as the number of shells included in the convergence is increased.

Before we go on, we should comment on our single-site results for V. In this case we find the rate of convergence to be extremely slow, with the moment decreasing at each iteration, indicating the onset of a magnetic instability. Our results indicate a very small moment for the V impurity within the single-site approximation. We find that the magnetic moment is estabilized when the Cu atoms are included in the convergence procedure (see Table I).

TABLE I. RS-LMTO-ASA and KKR-GF results for local magnetic moments (in units of μ_B) and local charge transfer (in excess of valence electrons at the given site) for systems consisting of V, Cr, Mn, or Fe impurities in Cu fcc hosts. We show local moments at the impurity (M_0) and at Cu atoms in the first four shells (M_1, M_2, M_3, and M_4) around the impurity. In the last two rows we show the charge transfer at the impurity (C_0) and at the first Cu neighbor (C_1) when only one shell of neighbors around the impurity is treated self-consistently.

	V		Cr		Mn		Fe	
	RS-LMTO-ASA	KKR-GF	RS-LMTO-ASA	KKR-GF	RS-LMTO-ASA	KKR-GF	RS-LMTO-ASA	KKR-GF
M_0	0.96	1.10	3.03	2.99	3.56	3.40	2.69	2.51
M_1	+0.0070	+0.0167	+0.0193	+0.0310	+0.0176	+0.0226	+0.0114	+0.0084
M_2	−0.0028	−0.0028	−0.0061	−0.0079	−0.0100	−0.0090	−0.0081	−0.0072
M_3	+0.0019	+0.0015	+0.0032	+0.0019	+0.0004	+0.0003	−0.0020	−0.0015
M_4	−0.0011	−0.0010	−0.0017	−0.0021	−0.0032	−0.0022	−0.0014	−0.0015
C_0	−0.53	−0.67	−0.40	−0.49	−0.34	−0.44	−0.20	−0.30
C_1	0.60	0.50	0.04	0.05	0.04	0.03	0.02	0.02

TABLE II. Local charge transfers (excess of valence electrons at the site) at the impurity (C_0) and four shells of Cu neighbors C_1, C_2, C_3, and C_4 around the impurity, obtained using the RS-LMTO-ASA scheme.

	V	Cr	Mn	Fe
C_0	−0.544	−0.410	−0.340	−0.208
C_1	0.058	0.044	0.036	0.023
C_2	0.000	−0.001	−0.001	−0.002
C_3	−0.006	−0.005	−0.004	−0.004
C_4	−0.004	−0.002	−0.001	0.000

The fact that the moment of V in a Cu host is close to an instability seems to be confirmed by calculations for pairs of $3d$ impurities as first neighbors in Cu. The Cr, Mn, and Fe pairs in a Cu host shown large magnetic moments at the impurity sites whether the V pairs are found to be nonmagnetic.[18] We should note that the convergence on charge was easily achieved for the single-site V.

In Table III (first row), we show RS-LMTO-ASA and KKR-GF results for the magnetic moment (SS) at the impurity for Cr, Mn, and Fe, using the single-site approximation. The second and third rows show values for moments at the impurity (M_0) and first Cu neighbor (M_1) for these same impurities, when both the impurity and the first shell of Cu neighbors are calculated self-consistently. The V impurity was not included for the reasons mentioned above. It is clear from Table III that the variations between single-site and first-neighbor converged results are much larger in the KKR-GF calculations than in the RS-LMTO-ASA. This also happens when charge transfer is considered. The KKR-GF results in the literature show an increase in the magnitude of the charge transfer at the impurity site, of roughly a factor of 2,[13] when the first shell of Cu atoms is included in the convergence. In contrast, our single-site results (−0.51 for V, −0.38 for Cr, −0.32 for Mn, and −0.20 for Fe) are in close agreement with those obtained with the inclusion of first neighbors, and shown in Table I.

The large variation observed in the KKR-GF results when the first shell of Cu atoms is included in the convergence is not intrinsic to the KKR-GR procedure. It can be understood if we analyze how the Madelung contribution and V_{es} were included in the RS-LMTO-ASA and KKR-GF calculations mentioned here. On the single-site KKR-GF calculation, the first Cu neighbors are taken to be neutral, while the impurity can have rather large charge transfers. In the RS-LMTO-ASA approach used here, the extra charge is placed in the first Cu shell when obtaining V_{es}, in order to simulate charge neutrality. When one includes the first neighbors in the self-consistent process, they immediately acquire a positive charge, which roughly compensates the excess charge on the impurity. The Madelung contribution due to this charge shifts the center of impurity band up by a considerable amount, expelling the charge and enhancing the charge transfer relative of the SS result. The single-site KKR-GF results could be easily improved, by introducing a procedure similar to the one used by us, when treating the Madelung contribution.

If one were to correct naively for the Madelung term by including the shift due to the charges of the first neighbors at the impurity site directly in the converged single-site results, the charge transfer would be unreasonably large for a metal. But, due to screening, if the convergence is achieved under the appropriate conditions, the results are not too different from those of the single-site calculation, where the charge in the Cu neighbors was neglected. We have just a factor-of-2 difference in the charge and a few percent discrepancy in the moments as can be seen from our discussion of the KKR-GF results. It is interesting to note that a similar effect makes the errors, introduced in our RS-LMTO-ASA calculations by the finite cutoff parameter $L_{\max}$ used in the recursion method, much smaller than we initially anticipated. We find that the differences in occupations when we change the value of the cutoff parameter in the recursion chain, from $L_{\max}=20$ to 18 or 19 are typically a little more than 5 millielectrons. But, due to screening, if we now try to achieve convergence of the system for $L_{\max}=18$, 19, and 20, the difference between these converged values will be less than 1 millielectron.

Finally, since the Hamiltonian used here is of the tight-binding form, we can easily verify whether a local Stoner criterion[7,19] is closely obeyed at the impurity site. To verify this, we determine the difference between the centers of the (up and down) d bands (ΔE_d), from our converged results and relate it to the d band polarization at the impurity site. We find that the ratio between the d magnetic moment at the impurity site and (ΔE_d) is almost constant for all impurities, of order of 0.066 Ry for Fe and Mn and of order of 0.062 Ry for Cr and V. These ratios are close to the value of the Stoner parameter for Fe, but slightly high when compared with the Stoner parameter of the other impurities.[7]

TABLE III. RS-LMTO-ASA and KKR-GF results for the local magnetic moment (in units of μ_B) for systems consisting of Cr, Mn, or Fe substitutional impurities in Cu fcc hosts. In the first row we show the magnetic moments at the impurity (SS) when a single-site calculation is performed. We also show the magnetic moment at the impurity (M_0) and first shell of Cu neighbors (M_1), when both the impurity and the first shell of Cu neighbors are treated self-consistently.

	Cr		Mn		Fe	
	RS-LMTO-ASA	KKR-GF	RS-LMTO-ASA	KKR-GF	RS-LMTO-ASA	KKR-GF
SS	3.05	3.06	3.58	3.23	2.71	2.30
M_0	3.03	3.09	3.57	3.44	2.70	2.55
M_1	0.02	0.03	0.02	0.02	0.01	0.01

V. CONCLUSIONS

We have presented a first-principles density-functional approach which allows us to obtain the electronic structure and related properties of locally perturbed metallic systems. The approach is a version of the recently developed RS-LMTO-ASA scheme, which was modified to treat local perturbations.

We have applied this RS-LMTO-ASA approach to study the behavior of $3d$ impurities (V, Cr, Mn, and Fe) in a fcc Cu host. The results are in excellent agreement with those obtained by the well-established KKR-GF formalism, confirming the accuracy of our method.

Sometimes because of external limitations, calculations are restricted to a single site. We show that the single-site results can be improved if the excess charge on the calculated site is compensated, in order to preserve charge neutrality, when calculating the Madelung contribution.

We note that the RS-LMTO-ASA scheme does not require symmetry and is extremely flexible. Therefore, the method presented in this paper can be applied to study interstitial impurities and can also be used in the presence of lattice relaxation. It is probably one of the most efficient approaches, if one wants to investigate local perturbations in complex hosts.

Finally, in the RS-LMTO-ASA scheme, the effort grows linearly with the number of sites with an inequivalent local density of states because the recursion procedures has to be repeated for each of these inequivalent sites. But the size of the computer used does not have to be increased. Therefore, the calculations do not require the use of supercomputers and the codes can be efficiently implemented on parallel machines.

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