Two ways to perform spin-polarized relativistic linear muffin-tin-orbital calculations

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Two spin-polarized relativistic versions of the linear muffin-tin-orbital method of band-structure calculations are presented. The first one is a pseudoperturbational method taking the effect of spin splitting only into account within the variational step. The second one treats spin polarization and spin-orbit coupling on the same level by making use of the proper solutions to the Dirac equation for a spin-dependent potential. Both approaches permit a detailed theoretical study of magnetocrystalline anisotropy effects. Results for the band structure, the spin and orbital magnetic moments and the conduction-band contribution to the hyperfine fields of Fe, Co, and Ni obtained by these methods are presented and compared to data obtained by an application of the spin-polarized version of the relativistic Korringa-Kohn-Rostoker method.

I. INTRODUCTION

There are quite a large number of interesting physical effects, such as, for example, the magnetooptic Kerr effect, which are caused by the simultaneous occurrence of spin polarization and spin-orbit coupling. As shown by the work of Brooks and other authors (see, for example, Ref. 1 and references therein), for systems containing heavy elements, even ground-state properties, such as the lattice constant or the bulk modulus, are obviously determined by a subtle interplay of relativistic effects and spin ordering. To allow a detailed description of the electronic structure for such situations, a number of band-structure methods has been extended during the last years. Besides the perturbational approaches,[2–5] one primarily has to mention the generalization of the Korringa-Kohn-Rostoker (KKR) formalism (SPR KKR) developed independently by Feder *et al.*[6] and Strange *et al.*[7] that permits one to treat spin polarization and all relativistic effects on the same footing.

Quite recently, also the linear rigorous cellular (LRC) method has been extended in a perturbational way[8,9] to deal with spin-polarized systems containing heavy elements. The most appealing property of the LRC method and of all other linear band-structure methods is that it is orders of magnitude faster than, for example, the highly accurate KKR method, while, in general, retaining sufficient numerical accuracy. In this paper a very simple way of incorporating spin-polarization effects in a conventional relativistic linear muffin-tin-orbital (RLMTO) calculation by perturbation theory is presented. A more accurate resulting band structure can, of course, be expected if the muffin-tin orbitals (MTO's) used in the variational step are set up by using proper solutions to the Dirac equation for a single-site, spin-dependent potential. A way to set up such spin-polarized relativistic MTO's is presented, leading to a spin-polarized fully-relativistic version of the LMTO method (SPR LMTO).

The paper is organized as follows. In the next section a brief discussion of the problem of treating spin-polarized systems within local-spin-density theory is given. For the sake of completeness, a short derivation of the RLMTO equations is summarized in the following section. A description of the perturbation RLMTO approach to the problem of spin polarization is given in Sec. II C, and in Sec. II D the SPR LMTO method is presented. A way of dealing with magnetocrystalline anisotropy within these both band-structure methods is outlined in Sec. II E. Results which have been obtained for the band structure, the magnetic moments, and hyperfine fields for ferromagnetic Fe, Co, and Ni are presented in Sec. III, together with a comparison to SPR KRR results.

II. SPIN-POLARIZED RELATIVISTIC LINEAR MUFFIN-TIN-ORBITAL CALCULATIONS

A. Dirac equation for a spin-dependent potential

The problem of dealing with magnetic systems in a completely relativistic way within density-functional theory has been discussed in the past by a number of authors (see, e.g., Ref. 10, and references therein). Quite analogously to the nonrelativistic case, a set of coupled Kohn-Sham-Dirac equations have been derived which describe the ground state of a relativistic many-electron system. This approach leads, strictly speaking, to a current density-functional theory with the electronic four-current density J^{μ} as the central quantity. The corresponding Hamiltonian is of the form

$$H=\underline{\alpha}\left[\frac{c}{i}\nabla+\mathbf{A}_H(J^{\mu})+\mathbf{A}_{\rm xc}(J^{\mu})\right]+\tfrac{1}{2}(\underline{\beta}-\underline{I})+V_H+V_{\rm xc}\ , \tag{1}$$

where the matrices $\underline{\alpha}_i$ $(i=1,2,3)$ and $\underline{\beta}$ are the standard Dirac matrices.[11] The indices H, x, and c indicate the Hartree, exchange, and correlation contributions, respectively, to the vector and scalar potentials V and $\mathbf{A}$, respectively.

Because of the great difficulties in dealing with this Hamiltonian, an alternative approach has been suggested[12] which is analogous to the nonrelativistic spin-density-functional formalism in assuming a hypothetic magnetic and/or exchange-correlation field coupling only to the spin of the electrons.

In the following sections two methods are presented which allow one to deal in a very efficient way with the corresponding Hamiltonian,

$$H=\frac{c}{i}\underline{\alpha}\cdot\nabla+\tfrac{1}{2}(\underline{\beta}-\underline{I})+\underline{V}(\mathbf{r}) , \tag{2}$$

for an ordered array of finite-ranged potential wells $\underline{V}(\mathbf{r})$ of the form

$$\begin{aligned}\underline{V}(\mathbf{r})&=V_H(r)+\overline{V}_{\rm xc}(r)+\underline{V}_{\rm spin}(\mathbf{r})\\&=V^0(r)+\underline{V}_{\rm spin}(\mathbf{r}) .\end{aligned} \tag{3}$$

Here, $\overline{V}_{\rm xc}(r)$ stands for the spin-averaged part of the exchange-correlation potential, while $\underline{V}_{\rm spin}(\mathbf{r})$ represents the spin-dependent part of $\underline{V}(\mathbf{r})$:

$$\begin{aligned}\underline{V}_{\rm spin}(\mathbf{r})&=\underline{\beta}\,\underline{\alpha}\left[\mathbf{B}_{\rm ext}+\frac{\partial E_{\rm xc}}{\partial \mathbf{m}(\mathbf{r})}\right]\\&=\underline{\beta}\,\underline{\alpha}\mathbf{B}_{\rm eff} ,\end{aligned} \tag{4}$$

with $\mathbf{B}_{\rm ext}$ an external field and $\underline{\alpha}$ the vector of the 4×4 Pauli matrices. While the first of the methods discussed below takes $\underline{V}_{\rm spin}(\mathbf{r})$ into account only in a perturbational way, the second one treats spin polarization due to $\underline{V}_{\rm spin}(\mathbf{r})$ and all relativistic effects on the same level by making use of the proper solutions to the Hamiltonian in Eq. (2) for a single potential well.

B. The RLMTO method

The relativistic LMTO method is a straightforward generalization of Andersen's[3] nonrelativistic band-structure technique that permits one to deal with paramagnetic systems containing heavy elements. It has been derived independently during the last few years by Christensen,[13] Godreche,[14] and Nemoshkalenko *et al.*[15] For the sake of completeness, the most important steps of this derivation are repeated here, adopting the notation and normalization convention as used by Skriver[16] in his monograph on the nonrelativistic LMTO method. For further details, see especially Refs. 15 and 16.

The starting points for the derivation of the RLMTO equations are the solutions $\phi_\Lambda(E,\mathbf{r})$ to the single-site Dirac equation [Eq. (2)] for a non-spin-dependent spherically symmetric potential $V(r)=V^0(r)$ of range S, where Λ stands for the set (κ,μ) of the relativistic quantum numbers κ and μ. The functions $\phi_\Lambda(E,\mathbf{r})$ are conventional bispinors,[11]

$$\phi_\Lambda(E,\mathbf{r})=i^l\begin{pmatrix} g_\kappa(E,r)\chi^\mu_\kappa(\hat{\mathbf{r}})\\ if_\kappa(E,r)\chi^\mu_{-\kappa}(\hat{\mathbf{r}})\end{pmatrix} , \tag{5}$$

with the radial functions $g_\kappa(E,r)$ and $f_\kappa(E,r)$ and the spin-angular functions

$$\chi^\mu_\kappa(\hat{\mathbf{r}})=\sum_{m_s=\pm1/2} C(l\tfrac{1}{2}j;\mu-m_s,m_s)Y_l^{\mu-m_s}(\hat{\mathbf{r}})\chi_{m_s} . \tag{6}$$

Normalization of $\phi_\Lambda(E,\mathbf{r})$ to 1 within the sphere of radius S results, for $\phi_\Lambda(E,\mathbf{r})$ and its energy derivative $\dot{\phi}_\Lambda(E,\mathbf{r})$, in the following relations:

$$(H-E)\phi_\Lambda(E,\mathbf{r})=0 , \tag{7}$$

$$(H-E)\dot{\phi}_\Lambda(E,\mathbf{r})=\phi_\Lambda(E,\mathbf{r}) , \tag{8}$$

$$\langle\phi_\Lambda(E,\mathbf{r})\,|\,\phi_\Lambda(E,\mathbf{r})\rangle=1 , \tag{9}$$

$$\langle\phi_\Lambda(E,\mathbf{r})\,|\,\dot{\phi}_\Lambda(E,\mathbf{r})\rangle=0 . \tag{10}$$

To match solutions to Eq. (2) inside the sphere to solutions outside the sphere, one introduces, analogously to the nonrelativistic case, the logarithmic derivative of $\phi_{\nu\Lambda}(\mathbf{r})$ and $\dot{\phi}_{\nu\Lambda}(\mathbf{r})$,

$$D_{\nu\kappa}=S\frac{cf_{\nu\kappa}(S)}{g_{\nu\kappa}(S)}-\kappa-1 , \tag{11}$$

$$D_{\dot{\nu}\kappa}=S\frac{c\dot{f}_{\nu\kappa}(S)}{\dot{g}_{\nu\kappa}(S)}-\kappa-1 , \tag{12}$$

where the index ν indicates that the energy has been fixed to some value E_ν. A trial function $\Phi_\Lambda(D,\mathbf{r})$ for $r\le S$ with an arbitrary logarithmic derivative D at $r=S$ is within Andersen's linear energy approximation (see, e.g., Ref. 16) given by an appropriate combination of $\phi_{\nu\Lambda}(\mathbf{r})$ and $\dot{\phi}_{\nu\Lambda}(\mathbf{r})$,

$$\Phi_\Lambda(D,\mathbf{r})=\phi_{\nu\Lambda}(\mathbf{r})+\omega_\kappa(D)\dot{\phi}_{\nu\Lambda}(\mathbf{r}) , \tag{13}$$

where the coefficient $\omega_\kappa(D)$,

$$\omega_\kappa(D)=-\frac{g_{\nu\kappa}(S)}{\dot{g}_{\nu\kappa}(S)}\frac{D-D_{\nu\kappa}}{D-D_{\dot{\nu}\kappa}} , \tag{14}$$

ensures that $\Phi_\Lambda(D,\mathbf{r})$ is continuous and differentiable at $r=S$. Within the atomic-sphere approximation (ASA) (see, e.g., Ref. 16), the potential in the interstitial region of a crystal can be chosen arbitrarily. The most convenient choice is to set $E-V(r)=0$, resulting in the decaying and diverging free-electron solutions $n_\Lambda(\mathbf{r})$ and $j_\Lambda(\mathbf{r})$. The functions $n_\Lambda(\mathbf{r})$ and $j_\Lambda(\mathbf{r})$ are the "relativistic" von Neumann and spherical Bessel functions for the wave number $\kappa=\sqrt{E-V}=0$ with the logarithmic derivative $-l-1$ and $+l$, respectively.[15]

A so-called muffin-tin orbital $\chi_\Lambda(\mathbf{r}-\mathbf{R})$ is now defined as a function centered at the lattice site $\mathbf{R}$, which is obtained if the decaying interstitial solution $n_\Lambda(\mathbf{r}-\mathbf{R})$ is augmented in the sphere centered at $\mathbf{R}$ by $\Phi_\Lambda(-l-1,\mathbf{r}-\mathbf{R})$ and by a linear combination of functions $\Phi_{\Lambda'}(+l',\mathbf{r}-\mathbf{R}')$ in all other spheres centered at $\mathbf{R}'$ in such a way that $\chi_\Lambda(\mathbf{r}-\mathbf{R})$ is continuous everywhere. The Bloch sum of such MTO's,

$$\chi^{\mathbf{k}}_\Lambda(\mathbf{r})=\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\chi_\Lambda(\mathbf{r}-\mathbf{R}) , \tag{15}$$

can be expressed by a one-center expansion for the sphere centered at the origin

$$\chi^{\mathbf{k}}_{\Lambda}(\mathbf{r})=\frac{\Phi_{\Lambda}(-l-1,\mathbf{r})}{\sqrt{S/2}g_{\kappa}(-l-1)} - \sum_{\Lambda'}\frac{\Phi_{\Lambda'}(l',\mathbf{r})}{2(2l'+1)\sqrt{S/2}g_{\kappa'}(l')}\sigma^{\mathbf{k}}_{\Lambda'\Lambda} \ . \tag{16}$$

Here, $g_{\kappa}(D)$ is the upper component of $\Phi_{\Lambda}(D,\mathbf{r})$ for $r=S$ and the $\sigma^{\mathbf{k}}_{\Lambda'\Lambda}$ are the so-called structure constants, which are related by

$$\sigma^{\mathbf{k}}_{\Lambda'\Lambda}=\sum_{m_s=\pm 1/2} C(l'\tfrac{1}{2}j';\mu'-m_s,m_s) \times S^{\mathbf{k}}_{l'\mu'-m_s,l\mu-m_s}C(l\tfrac{1}{2}j;\mu-m_s,m_s) \tag{17}$$

to the conventional nonrelativistic structure constants $S^{\mathbf{k}}_{l'm_l',lm_l}$.[15]

Using the Bloch sum of MTO's as basis functions for an application of the Rayleigh-Ritz variational principle, one ends up with the generalized eigenvalue problem

$$\sum_{\Lambda}(H^{\mathbf{k}}_{\Lambda'\Lambda}-E^{j\mathbf{k}}O^{\mathbf{k}}_{\Lambda'\Lambda})\alpha^{j\mathbf{k}}_{\Lambda}=0 \tag{18}$$

for the eigenvalues $E^{j\mathbf{k}}$ and the eigenvectors $\alpha^{j\mathbf{k}}_{\Lambda}$, specifying the corresponding Bloch wave functions. Because the matrix elements of the operators $(H-E)$ and 1 for the functions $\Phi_{\Lambda}(D,\mathbf{r})$ have the simple form

$$\langle\Phi_{\Lambda'}(D',\mathbf{r})\,|\,(H-E)\,|\,\Phi_{\Lambda}(D,\mathbf{r})\rangle=\omega_{\kappa}(D)\delta_{\Lambda'\Lambda} \ , \tag{19}$$

$$\langle\Phi_{\Lambda'}(D',\mathbf{r})\,|\,\Phi_{\Lambda}(D,\mathbf{r})\rangle=[1+\omega_{\kappa}(D')\omega_{\kappa}(D)\langle\dot{\phi}^2_{\nu\kappa}\rangle]\delta_{\Lambda'\Lambda} \ , \tag{20}$$

the elements of the Hamilton and overlap matrices in Eq. (18), $H^{\mathbf{k}}_{\Lambda'\Lambda}$ and $O^{\mathbf{k}}_{\Lambda'\Lambda}$, respectively, can be expressed by the elements of the structure-constant matrix $\sigma^{\mathbf{k}}_{\Lambda'\Lambda}$ and the four so-called potential parameters: $\omega(-)$, $\Phi(-)$, $\Phi(-)/\Phi(+)$, and $\langle\dot{\phi}^2_{\nu}\rangle$, where $+$ and $-$ stand for $+l$ and $-l-1$, respectively.

Explicit formulas for $H^{\mathbf{k}}_{\Lambda'\Lambda}$ and $O^{\mathbf{k}}_{\Lambda'\Lambda}$ can simply be obtained from their nonrelativistic counterparts[16] by the substitutions $L=(l,m)\rightarrow\Lambda=(\kappa,\mu)$ and $\Phi_l(D)\rightarrow g_{\kappa}(D)$, resulting, of course, in a doubling of the size of the matrices. Finally, one should mention that the relativistic so-called combined-correction terms,[16] which "cure" the errors introduced by the ASA to some extent, are related to their nonrelativistic counterparts by a relation analogous to Eq. (17).

C. Perturbational approach to the spin-polarized relativistic band-structure problem

The easiest way to deal with the full Hamiltonian operator for a spin-dependent potential is to apply perturbation theory or, in other words, take account of the spin-dependent part $\underline{V}_{\text{spin}}(\mathbf{r})$ of $\underline{V}(\mathbf{r})$ only within the variational step. This means that an approximate RLMTO Hamiltonian matrix $H^{\mathbf{k}}_{\Lambda'\Lambda}$ for a spin-dependent potential is the sum of the matrix $H^{\mathbf{k}0}_{\Lambda'\Lambda}$, which is evaluated for $V^0(r)=\underline{V}(\mathbf{r})-\underline{V}_{\text{spin}}(\mathbf{r})$ as for the non-spin-polarized case, and the matrix

$$V^{\mathbf{k}}_{\Lambda'\Lambda}=\langle\chi^{\mathbf{k}}_{\Lambda'}\,|\,\underline{V}_{\text{spin}}(\mathbf{r})\,|\,\chi^{\mathbf{k}}_{\Lambda}\rangle \ . \tag{21}$$

As for $H^{\mathbf{k}0}_{\Lambda'\Lambda}$, this matrix can easily be expressed by matrix elements of $\underline{V}_{\text{spin}}(\mathbf{r})$ for the functions $\Phi_{\Lambda}(D,\mathbf{r})$. These, in turn, are given by

$$\begin{aligned}\langle\Phi_{\Lambda'}(D',\mathbf{r})\,|\,\underline{V}_{\text{spin}}(\mathbf{r})\,|\,\Phi_{\Lambda}(D,\mathbf{r})\rangle=&G(\kappa',\kappa,\mu)[B\{g_{\kappa'},g_{\kappa}\}+\omega_{\kappa}(D)B\{g_{\kappa'},\dot{g}_{\kappa}\}+\omega_{\kappa'}(D')B\{\dot{g}_{\kappa'},g_{\kappa}\}+\omega_{\kappa'}(D')\omega_{\kappa}(D)B\{\dot{g}_{\kappa'},\dot{g}_{\kappa}\})]\\&+G(-\kappa',-\kappa,\mu)[B\{f_{\kappa'},f_{\kappa}\}+\omega_{\kappa}(D)B\{f_{\kappa'},\dot{f}_{\kappa}\}+\omega_{\kappa'}(D')B\{\dot{f}_{\kappa'},f_{\kappa}\}\\&+\omega_{\kappa'}(D')\omega_{\kappa}(D)B\{\dot{f}_{\kappa'},\dot{f}_{\kappa}\}] \ ,\end{aligned} \tag{22}$$

with

$$\langle\chi^{\mu'}_{\kappa'}\,|\,\sigma_z\,|\,\chi^{\mu}_{\kappa}\rangle=\delta_{\mu\mu'}G(\kappa',\kappa,\mu)=\delta_{\mu\mu'}\begin{cases}-\mu/(\kappa+\frac{1}{2}), & \kappa=\kappa'\\ -\{1-[\mu/(\kappa+\frac{1}{2})]^2\}^{1/2}, & \kappa=-\kappa'-1\\ 0, & \text{otherwise}\end{cases} \tag{23}$$

and

$$B\{\dot{g}_{\kappa'},g_{\kappa}\}\int dr\,r^2B_{\text{eff}}(r)\dot{g}_{\nu\kappa'}(r)g_{\nu\kappa}(r) \ , \tag{24}$$

and analogously for all other functions $B\{\alpha_{\kappa'},\beta_{\kappa}\}$ with $\alpha,\beta=(g,\dot{g},f,\dot{f})$.

Due to the properties of the angular part $\langle\chi^{\mu'}_{\kappa'}\,|\,\sigma_z\,|\,\chi^{\mu}_{\kappa}\rangle$, the matrix elements

$$\langle\Phi_{\Lambda'}(D',\mathbf{r})\,|\,\underline{V}_{\text{spin}}(\mathbf{r})\,|\,\Phi_{\Lambda}(D,\mathbf{r})\rangle$$

are only diagonal in l and μ, which means, apart from the coupling between functions with $\kappa=\kappa'$, there is a coupling for $\kappa=-\kappa'-1$. However, this coupling produces no remarkable difficulties to setting up the matrix $V^{\mathbf{k}}_{\Lambda'\Lambda}$. Because all further steps within this perturbational approach are completely identical to a conventional RLMTO calculation, this method provides a very simple way to perform spin-polarized relativistic band-structure calculations. Furthermore, ignoring the spin dependence of the potential in the interstitial region, one can go, just as within the RLMTO method, beyond the ASA by using the combined-correction terms.

Obviously, the perturbational approach outlined above is quite similar to the method suggested by Andersen[3] to take spin-orbit coupling within a nonrelativistic LMTO calculation into account by adding to the LMTO Hamiltonian in the (l,m_l,m_s) representation the matrix of the spin-orbit operator $\xi\mathbf{l}\cdot\mathbf{s}$. Relativistic effects, other than spin-orbit coupling, are taken into account within that method by performing a scalar-relativistic calculation of the wave functions.

D. The SPR LMTO method

A more accurate solution to the spin-polarized relativistic band-structure problem than the perturbational methods allow will, of course, be obtained by setting up the relativistic MTO's by using proper solutions to the single-site Dirac equation for a spin-dependent potential $\underline{V}(\mathbf{r})$. Such an approach will be described in the following.

As shown by Feder *et al.*,[3] Strange *et al.*,[7] and also Cortona *et al.*,[17] the spin-dependent potential in the Dirac equation, in principle, results in sets of an infinite number of coupled equations for the radial functions. However, one can give arguments[6] that it is allowed to neglect the coupling between all radial functions apart from that between those with $\Delta l=0$ and $\Delta\mu=0$. As pointed out by Cortona *et al.*,[17] and as can be seen from the discussion above, this simplifying step can also be justified by perturbational arguments. It is, however, not necessary for the further derivation, which could also include more complicated coupling mechanisms. Restricting the coupling to $\Delta l=0$ and $\Delta\mu=0$, a proper solution to Eq. (2) has the form

$$\phi_i(E,\mathbf{r})=\phi_{\Lambda i}(E,\mathbf{r})+\phi_{\bar{\Lambda} i}(E,\mathbf{r}) , \tag{25}$$

where $\Lambda=(\kappa,\mu)$, $\bar{\Lambda}=(-\kappa-1,\mu)$, and i numbers the various independent solutions to Eq. (2). In contrast to the Dirac equation for a spin-dependent potential, the functions $\phi_i(E,\mathbf{r})$ have no unique spin-angular character—apart from the cases $|\mu|=j$, $j=l+\frac{1}{2}$, where there is only one term on the right-hand side of Eq. (25). Obviously, there are two solutions—$\phi_i(E,\mathbf{r})$ and $\phi_{i'}(E,\mathbf{r})$—which contain functions of a given spin-angular character Λ.

Normalizing $\phi_i(E,\mathbf{r})$ to 1 within the sphere of radius S, $\phi_i(E,\mathbf{r})$ and its energy derivative $\dot{\phi}_i(E,\mathbf{r})$ satisfy, analogously to Eqs. (7)–(10), the relations

$$(H-E)\phi_i(E,\mathbf{r})=0 , \tag{26}$$

$$(H-E)\dot{\phi}_i(E,\mathbf{r})=\phi_i(E,\mathbf{r}) , \tag{27}$$

$$\langle\phi_i(E,\mathbf{r})\,|\,\phi_i(E,\mathbf{r})\rangle=1 , \tag{28}$$

$$\langle\phi_i(E,\mathbf{r})\,|\,\dot{\phi}_i(E,\mathbf{r})\rangle=0 . \tag{29}$$

In principle, one could go on completely analogously to the conventional LMTO method[16] to construct spin-polarized relativistic MTO's. This approach results, however, in a very inconvenient form of the Hamiltonian and overlap matrix elements. An alternative way to set up the MTO's is simply to augment smoothly the interstitial solutions $n_\Lambda(\mathbf{r})$ within the central cell by $\Phi_\Lambda(-l-1,\mathbf{r})$ and in all other spheres by linear combinations of $\Phi_{\Lambda'}(+l',\mathbf{r})$. These functions $\Phi_\Lambda(D,\mathbf{r})$ are now found by smoothly matching linear combinations of the solutions $\phi_{\nu i}(\mathbf{r})$ and their energy derivatives $\dot{\phi}_{\nu i}(\mathbf{r})$ containing functions of spin-angular character Λ [see Eq. (25)] to $n_\Lambda(\mathbf{r})$ for $D=-l-1$ or $j_\Lambda(\mathbf{r})$ for $D=+l$, respectively, where again the index ν specifies a fixed energy E_ν. The corresponding matching condition in the case of $n_\Lambda(\mathbf{r})$ for $r=S$ then reads

$$1=\phi_{\nu\Lambda i}\alpha_{i\Lambda}(-)+\phi_{\nu\Lambda i'}\alpha_{i'\Lambda}(-)+\dot{\phi}_{\nu\Lambda i}\beta_{i\Lambda}(-)+\dot{\phi}_{\nu\Lambda i'}\beta_{i'\Lambda}(-) , \tag{30}$$

$$0=\phi_{\nu\bar{\Lambda}' i}\alpha_{i\Lambda}(-)+\phi_{\nu\bar{\Lambda}' i'}\alpha_{i'\Lambda}(-)+\dot{\phi}_{\nu\bar{\Lambda}' i}\beta_{i\Lambda}(-)+\dot{\phi}_{\nu\bar{\Lambda}' i'}\beta_{i'\Lambda}(-) , \tag{31}$$

$$\frac{-l-1}{S}=\phi'_{\nu\Lambda i}\alpha_{i\Lambda}(-)+\phi'_{\nu\Lambda i'}\alpha_{i'\Lambda}(-)+\dot{\phi}'_{\nu\Lambda i}\beta_{i\Lambda}(-)+\dot{\phi}'_{\nu\Lambda i'}\beta_{i'\Lambda}(-) , \tag{32}$$

$$0=\phi'_{\nu\bar{\Lambda}' i}\alpha_{i\Lambda}(-)+\phi'_{\nu\bar{\Lambda}' i'}\alpha_{i'\Lambda}(-)+\dot{\phi}'_{\nu\bar{\Lambda}' i}\beta_{i\Lambda}(-)+\dot{\phi}'_{\nu\bar{\Lambda}' i'}\beta_{i'\Lambda}(-) . \tag{33}$$

In Eqs. (30)–(33), $(-)$ indicates the logarithmic derivative $-l-1$ of $n_\Lambda(\mathbf{r})$ and the prime indicates the radial derivation $\partial/\partial r$. Analogous equations are obtained for $j_\Lambda(\mathbf{r})$ $(D=+l)$, which can easily be solved for the new potential parameters $\alpha_{i\Lambda}(D)$ and $\beta_{i\Lambda}(D)$. For a vanishing spin-dependent potential $\underline{V}_{\text{spin}}(\mathbf{r})$, the label i can obviously be replaced by Λ because the functions with spin-angular character $\bar{\Lambda}$ will not occur in Eq. (25) (no coupling). In that special case the new potential parameters $\alpha_{i\Lambda}(D)$ and $\beta_{i\Lambda}(D)$ are simply a different way to write the conventional potential parameters,

$$\omega(-)=\beta(-)/\alpha(-) , \tag{34}$$

$$\Phi(-)=1/\alpha(-) , \tag{35}$$

$$\Phi(-)/\Phi(+)=\alpha(+)/\alpha(-) . \tag{36}$$

As for the perturbational approach, all further steps to set up the SPR LMTO equations are completely analogous to the non-spin-polarized case. The structure of the corresponding new Hamiltonian and overlap matrices, $H^{\mathbf{k}}_{\Lambda'\Lambda}$ and $O^{\mathbf{k}}_{\Lambda'\Lambda}$, respectively, is identical to that of the matrix $V^{\mathbf{k}}_{\Lambda'\Lambda}$ occurring within the perturbational approach [see Eq. (21)]. This stems from the fact that the matrix elements of $(H-E)$ for the functions $\Phi_\Lambda(D,\mathbf{r})$ and their overlap matrix elements are only diagonal in l and μ but not in κ. Expressed by the potential parameters $\alpha_{i\Lambda}(D)$ and $\beta_{i\Lambda}(D)$, these matrix elements are given by

$$\langle \Phi_{\Lambda'}(D') \mid \Phi_{\Lambda}(D) \rangle = \sum_{i,i'} [\alpha_{i'\Lambda'}(D')\alpha_{i\Lambda}(D)\langle \phi_{i'} \mid \phi_i \rangle + \alpha_{i'\Lambda'}(D')\beta_{i\Lambda}(D)\langle \phi_{i'} \mid \dot{\phi}_i \rangle + \beta_{i'\Lambda'}(D')\alpha_{i\Lambda}(D)\langle \dot{\phi}_{i'} \mid \phi_i \rangle + \beta_{i'\Lambda'}(D')\beta_{i\Lambda}(D)\langle \dot{\phi}_{i'} \mid \dot{\phi}_i \rangle] , \tag{37}$$

$$\langle \Phi_{\Lambda'}(D') \mid (H-E) \mid \Phi_{\Lambda}(D) \rangle = \sum_{i,i'} [\alpha_{i'\Lambda'}(D')\beta_{i\Lambda}(D)\langle \phi_{i'} \mid \phi_i \rangle + \beta_{i'\Lambda'}(D')\beta_{i\Lambda}(D)\langle \dot{\phi}_{i'} \mid \phi_i \rangle] . \tag{38}$$

To evaluate expectation values of physical operators, it is, of course, more convenient to express the occurring matrix elements in terms of the single-site solutions ϕ_i [Eq. (25)] and their energy derivatives $\dot{\phi}_i$ instead of using the one-center expansions of the Bloch sum of MTO's, $\chi^{\mathbf{k}}_{\Lambda}(\mathbf{r})$, which have the same form as in Eq. (16) for the non-spin-polarized case. This means that one should write the Bloch wave functions $\Psi^{j\mathbf{k}}(\mathbf{r})$ as the expansion

$$\Psi^{j\mathbf{k}}(\mathbf{r}) = \sum_i [A_i^{j\mathbf{k}}\phi_i(\mathbf{r}) + B_i^{j\mathbf{k}}\dot{\phi}_i(\mathbf{r})] , \tag{39}$$

and not in terms of the eigenvectors $\alpha^{j\mathbf{k}}_{\Lambda}$, i.e., as

$$\Psi^{j\mathbf{k}}(\mathbf{r}) = \sum_{\Lambda} \alpha^{j\mathbf{k}}_{\Lambda}\chi^{\mathbf{k}}_{\Lambda}(\mathbf{r}) . \tag{40}$$

Although it is a bit tedious, it is straightforward to express the expansion coefficients $A_i^{j\mathbf{k}}$ and $B_i^{j\mathbf{k}}$ in terms of the eigenvectors, just as it is done in the non-spin-polarized case [see Ref. 16, Eq. (6.30)].

Finally, one should mention, again, that one can go beyond the ASA by using the combined-correction terms, just as within the conventional RLMTO method.

E. Treatment of magnetocrystalline anisotropy

It is well known that the simultaneous occurrence of spin polarization and spin-orbit coupling gives rise to the magnetocrystalline anisotropy in the electron band structure. In the case of a cubic lattice this means, for example, that the dispersion relations for the wave vector $\mathbf{k}$ along the x axis are different from those along the z axis if the magnetization points along the z axis. So far, this special orientation of the magnetization, which enters the Dirac equation (2), has tacitly used in the above formalism. To fix the magnetization along the z axis of the crystal frame of reference is, however, an unnecessary restriction. The direction of the magnetization inside an atomic sphere specifies a local frame of reference (or at least its z axis) which might differ from that of the crystal. The conventional way to deal with this case within the KKR method[18,19] is to transform the single-site t matrix $t_{\Lambda\Lambda'}$ (see, e.g., Ref. 7) by an unitary transformation from the local frame of reference to the crystal frame. Of course, one can also go the opposite way. This means one can transform the structure constants by performing the transformation

$$\sigma^{\mathbf{k},\mathrm{loc}}_{\Lambda'\Lambda} = \sum_{\Lambda'',\Lambda'''} D_{\Lambda\Lambda''}(\alpha,\beta,\gamma)\sigma^{\mathbf{k},\mathrm{cryst}}_{\Lambda''\Lambda'''}D^{\times}_{\Lambda'''\Lambda'}(\alpha,\beta,\gamma) , \tag{41}$$

where (α,β,γ) are the Euler angles which specify the rotation of the crystal frame of reference to the local one. From a practical point of view, it is more convenient to transform the nonrelativistic structure constants $S^{\mathbf{k}}_{l'-m_l',lm_l}$ and to set up the relativistic ones according to Eq. (17) only after this transformation. Explicit formulas for the "nonrelativistic" rotation matrices $D_{LL'}(\alpha,\beta,\gamma)$ [$L=(l,m_l)$] can be found in Ref. 20.

The local structure constants $\sigma^{\mathbf{k},\mathrm{loc}}_{\Lambda'\Lambda}$ have to be used to set up the MTO's or the Hamiltonian and overlap matrices $H^{\mathbf{k}}_{\Lambda'\Lambda}$ and $O^{\mathbf{k}}_{\Lambda'\Lambda}$, respectively. This holds for using the perturbational RLMTO as well as for the SPR LMTO method in calculating a spin-polarized relativistic band structure. If for a many-atom unit cell the direction of the magnetization differs for the various atoms of the cell,[21] one can take this additional complication into account by constructing different sets of "local" structure constants.

III. RESULTS AND DISCUSSION

In this section results for the ferromagnetic metals Fe, Co, and Ni are presented, which have been obtained by the perturbational RLMTO as well as the SPR LMTO method within the atomic-sphere approximation (ASA). Both methods have been implemented by making use of Skriver's nonrelativistic LMTO program package,[16] together with the radial differential equation solver taken from Loucks's monograph on the augmented-plane-wave (APW) method[22] or supplied by Strange,[7] respectively. All calculations were performed non-self-consistently using the potentials tabulated by Moruzzi *et al.*[23] Preliminary results of these calculations have been published elsewhere.[24]

Of course, the overall features of the band structure of the relatively light elements Fe, Co, and Ni do not change dramatically when all relativistic effects are taken into account within a calculation. Nevertheless, as shown below there are non-negligible effects on the magnetic properties for these metals. To calculate the spin and orbital moments and the hyperfine field, we use the following formulas:[20,25]

$$\mu_{\mathrm{spin}} = \mu_B \sum_{j,\mathbf{k}} \langle \Psi^{j\mathbf{k}} \mid \underline{\beta}\,\underline{\sigma}_z \mid \Psi^{j\mathbf{k}} \rangle \Theta(E_F - E_{j\mathbf{k}}) , \tag{42}$$

$$\mu_{\mathrm{orb}} = \mu_B \sum_{j,\mathbf{k}} \langle \Psi^{j\mathbf{k}} \mid \underline{\beta}\,\underline{l}_z \mid \Psi^{j\mathbf{k}} \rangle \Theta(E_F - E_{j\mathbf{k}}) , \tag{43}$$

$$B_{\mathrm{hyp}} = \mu_{\mathrm{nuc}}^{-1} \sum_{j,\mathbf{k}} \langle \Psi^{j\mathbf{k}} \mid e\underline{\boldsymbol{\alpha}}\,\mathbf{A}_{\mathrm{nuc}} \mid \Psi^{j\mathbf{k}} \rangle \Theta(E_F - E_{j\mathbf{k}}) , \tag{44}$$

where E_F is the Fermi energy and $\mathbf{A}_{\mathrm{nuc}}$ is the vector potential due to the nuclear magnetic dipole moment. Because our calculations have been performed non-self-consistently, the orbital magnetic moment is only a

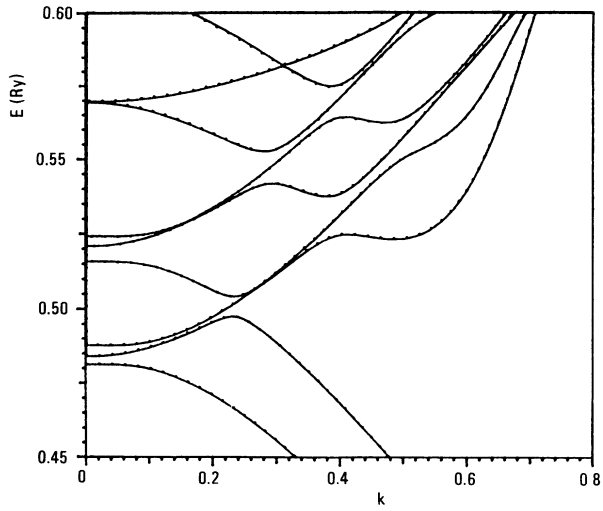

FIG. 1. Band structure of Ni for $\mathbf{k}\|[100]$ and the magnetization $\mathbf{M}\|[001]$ as obtained by the perturbational RLMTO (· · · ·) and SPR LMTO (——) methods. Here, as in Figs. 2 and 3, only the $|\mathbf{k}|$ range from 0 to $0.8(2\pi/a)$ is displayed.

consequence of the unquenching of the orbital magnetic momentum by the spin-orbit coupling. Within a nonrelativistic calculation μ_{orb} would be zero. One should, however, mention that the formula for μ_{orb} in Eq. (43) is only an approximation to the full relativistic orbital moment (see, e.g., Refs. 25 and 26). In contrast to a nonrelativistic treatment of the hyperfine interaction, Eq. (44) also results in contributions stemming from non-s electrons—again as a consequence of the spin-orbit coupling.

TABLE I. Magnetic moments in μ_B for $\mathbf{M}\|[001]$ for Fe, Co, and Ni as calculated by the perturbational RLMTO and SPR LMTO methods.

	Pert. RLMTO 1 E panel	SPR LMTO 1 E panel	SPR LMTO 4 E panels
$\mu_{\text{spin}}^{\text{Fe},s}$	−0.012	−0.011	−0.011
$\mu_{\text{spin}}^{\text{Fe},p}$	−0.050	−0.052	−0.050
$\mu_{\text{spin}}^{\text{Fe},d}$	2.147	2.189	2.185
$\mu_{\text{orb}}^{\text{Fe},p}$	0.0003	0.0001	0.0001
$\mu_{\text{orb}}^{\text{Fe},d}$	0.0383	0.0410	0.0411
$\mu_{\text{spin}}^{\text{Co},s}$	−0.015	−0.014	−0.014
$\mu_{\text{spin}}^{\text{Co},p}$	−0.056	−0.057	−0.056
$\mu_{\text{spin}}^{\text{Co},d}$	1.593	1.611	1.607
$\mu_{\text{orb}}^{\text{Co},p}$	0.0006	0.0007	0.0007
$\mu_{\text{orb}}^{\text{Co},d}$	0.0654	0.0667	0.0670
$\mu_{\text{spin}}^{\text{Ni},s}$	−0.006	−0.005	−0.005
$\mu_{\text{spin}}^{\text{Ni},p}$	−0.027	−0.027	−0.027
$\mu_{\text{spin}}^{\text{Ni},d}$	0.601	0.603	0.604
$\mu_{\text{orb}}^{\text{Ni},p}$	0.0004	0.0004	0.0004
$\mu_{\text{orb}}^{\text{Ni},d}$	0.0476	0.0481	0.0482

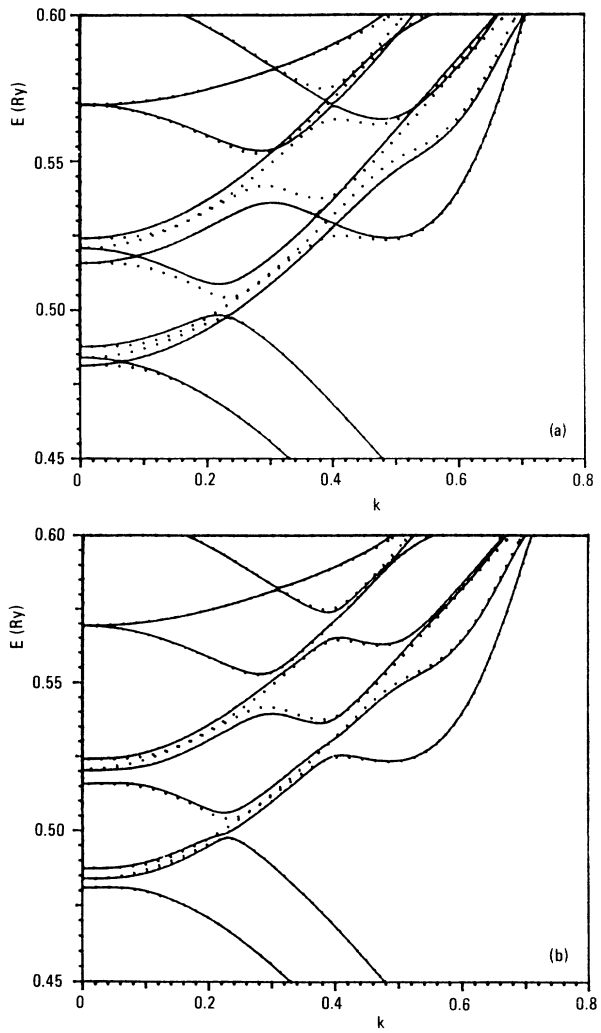

FIG. 2. Band structure of Ni for $\mathbf{k}\|[100]$, $\mathbf{M}\|[001]$ (· · · ·) and (a) $\mathbf{M}\|[100]$ (——) and (b) $\mathbf{M}\|[111]$ (——), respectively, as obtained by the SPR LMTO method.

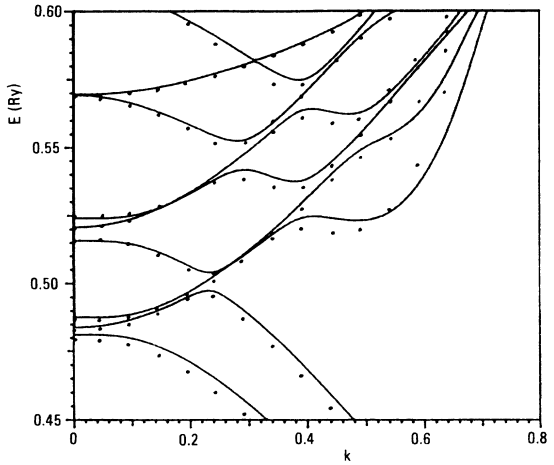

FIG. 3. Band structure of Ni for $\mathbf{k}\|[100]$ and $\mathbf{M}\|[001]$ as obtained by the SPR LMTO (——) and the SPR KKR (· · · ·) methods.

TABLE II. Angular-momentum-decomposed spin and orbital magnetic moments in μ_B and hyperfinefields in kG (only conduction band) for **M**||[001] for Fe, Co, and Ni as calculated by the (a) SPR LMTO, (b) SPR KKR (Ref. 24), and (c) the nonrelativistic KKR (Ref. 23) method.

	Fe			Co			Ni		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
μ^s_{spin}	−0.011	−0.010		−0.014	−0.015		−0.005	−0.002	
μ^p_{spin}	−0.050	−0.047		−0.056	−0.053		−0.026	−0.022	
μ^d_{spin}	2.185	2.140		1.607	1.578		0.604	0.622	
μ_{spin}	2.123	2.083	2.150	1.537	1.510	1.560	0.572	0.598	0.590
μ^p_{orb}	0.000	0.000		0.001	0.000		0.000	0.000	
μ^d_{orb}	0.041	0.056		0.067	0.069		0.048	0.046	
μ_{orb}	0.041	0.056		0.068	0.069		0.049	0.046	
B^s_{hyp}	−50.3	−42.1		−70.3	−72.0		−24.8	−5.9	
B^p_{hyp}	0.7	0.7		1.6	1.7		0.8	0.6	
B^d_{hyp}	14.3	23.9		40.7	47.6		40.3	36.9	
B_{hyp}	−35.3	−17.4		−28.0	−22.7		16.2	31.7	

Results for the band structure of Ni using the perturbational RLMTO and the SPR LMTO methods are shown together in Fig. 1. Obviously, the agreement of both sets of bands is surprisingly good. This holds also for the corresponding magnetic moments, which have been decomposed into their angular-momentum contributions and are summarized in Table I. From these results one can conclude that the perturbational RLMTO method guarantees, for a wide range of applications, sufficient numerical accuracy. The results in columns 1 and 2 of Table I have been obtained using only one energy panel and fixing E_ν to 0.4 Ry independent of the quantum number κ. The moments in column 3 emerged from calculations using four energy panels with E_ν fixed to 0.1, 0.3, 0.5, and 0.7 Ry, respectively. Obviously, in calculating energy-integrated quantities it seems to be sufficient to use only one energy panel.

The influence of the magnetocrystalline anisotropy on the band structure of Ni is demonstrated in Figs. 2(a) and 2(b), where the dispersion relations for three different orientations of the magnetization are shown. As can be seen, the hybridization and crossing of bands strongly depends on the orientation of the magnetization. Nevertheless, in the case of Ni the anisotropy energy is, of course, rather small.[19]

To check the accuracy of the SPR LMTO method, the results for Ni obtained with the SPR LMTO method are compared to SPR KKR results in Fig. 3. Obviously, all qualitative features for the two sets of bands, such as lifting of degeneracies, crossing, and avoiding of bands, completely agree. This has also been found for all other cases studied, ensuring the reliability of the SPR LMTO method. Also, the quantitative agreement of the both sets of bands in Fig. 3 is quite satisfying. The most pronounced discrepancies occur at higher energies. This finding does not result from the fixing of E_ν at 0.4 Ry, but should be ascribed to the neglection of the combined-correction terms. In Table II the magnetic moments and the hyperfine fields for Fe, Co, and Ni obtained by the SPR LMTO and SPR KKR methods are summarized. For the magnetic moments, which have again been decomposed into their l contributions, the agreement is very satisfying. This does not hold, however, for the hyperfine fields, which in some cases differ rather strongly. Because the energy-dependent integrand that occurs in a calculation of the hyperfine fields by the SPR KKR method is rather "spiky," even if one works with an energy contour far in the complex plane, it is assumed that the SPR LMTO results for B_{hyp} are more reliable than the SPR KKR data.[25]

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