PHYSICAL REVIEW B VOLUME 57, NUMBER 22 1 JUNE 1998-II

Real-space approach to the calculation of magnetocrystalline anisotropy in metals

S. V. Beiden
Department of Physics, University of Sheffield, Sheffield, United Kingdom

W. M. Temmerman and Z. Szotek
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

G. A. Gehring
Department of Physics, University of Sheffield, Sheffield, United Kingdom

G. M. Stocks, Yang Wang, D. M. C. Nicholson, and W. A. Shelton
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

H. Ebert
Institute for Physical Chemistry, University of München, Theresienstrasse 37, D-80333 München, Germany

(Received 3 November 1997)

We have implemented the fully relativistic and spin-polarized extension of the locally self-consistent multiple-scattering method. We have calculated the spin and orbital magnetic moments and magnetocrystalline anisotropy energy of Fe, Ni, and Co in the face-centered-cubic (fcc) and hexagonal-close-packed (hcp) crystal structures. We have obtained fast convergence of these quantities in real space. Moreover, these results compare favorably with the results of conventional **k**-space methods. [S0163-1829(98)00722-X]

I. INTRODUCTION

The consideration of magnetic interactions in solids *relativistically* leads to magnetocrystalline anisotropy that is one of the important physical quantities that determine the technical magnetic properties of bulk metallic alloys[1] and thin films[2–4] and is also of importance to the physics of heavy fermion systems.[5] So far, first-principles quantum-mechanical calculations of the magnetocrystalline anisotropy have nearly all been carried out by using **k**-space methods designed for periodic systems. This however considerably limits the range of applications. In this paper we advocate use of a real-space method that offers the hope of allowing us to perform spin-polarized relativistic total-energy calculations in complex systems such as disordered alloys, thin films, magnetic multilayers, and interfaces where nonperiodic effects, such as compositional inhomogeneities, lattice relaxations, strains, and noncollinear magnetizations, are important. Moreover, in the case of periodic systems, a real-space approach might provide a way of analyzing such properties as orbital magnetic moment and even such subtle relativistic effects as the magnetocrystalline anisotropy.

In this paper we present the spin-polarized relativistic (SPR) implementation of the real-space locally self-consistent multiple-scattering (LSMS) method.[6,7] A preliminary account of this work has recently been published.[8] Although in this paper we only present results for elemental metals, the resulting SPR-LSMS method has the property that computational effort will scale linearly $[O(N)]$, with system size N, in the same manner as the standard nonrelativistic LSMS method. Consequently, the SPR-LSMS can be trivially extended to large ($\sim$ hundreds of atoms) systems using currently available massively parallel computers.

In the LSMS method it is assumed that the Green function for each site in the solid can be obtained by considering only multiple-scattering effects from a finite cluster of atoms, referred to as the local interaction zone (LIZ), surrounding that site. In the LSMS method the LIZ size is the central convergence parameter rather than **k**-point sampling as in conventional reciprocal space band-structure methods. As has been pointed out previously, the convergence rate with respect to LIZ size depends on the quantity that is being calculated. For example, the electronic charge density is much more rapidly convergent than the total energy. For fcc and bcc transition metals, a LIZ consisting of one or two nearest-neighbor shells (NNS's) is sufficient to converge the electronic charge density while, for simple cases (e.g., Cu, Zn), a minimum of five or six NNS's are required to converge the total energy, and for more difficult cases (e.g., Mo) an even larger LIZ and the use of a finite temperature, Harris-Foulkes-like, free-energy functional[7] and a fictitious electron temperature of a few thousand degrees is required to obtain convergence. For the magnetic moments of transition metals calculated with the standard nonrelativistic local spin-density approximation, those of Fe and Co are obtained accurately with just two or three NNS's, while no magnetic moment is found for Ni with a LIZ of less than four NNS's after which it converges rapidly to the result obtained using conventional band-structure methods. Here, we make a detailed study of the convergence as a function of LIZ size of the spin and orbital moments and magnetocrystalline anisotropy energy (MAE) of elemental Fe (bcc), Ni (fcc), and Co (fcc and hcp) using the SPR-LSMS method and compare the results with standard methods.

The magnetocrystalline anisotropy energy of a transition metal is a notoriously difficult quantity to calculate in **k** space.[9–12] In some calculations in excess of 300 000 **k** points were required to converge the necessary Brillouin zone (BZ) integrations.[12] Special procedures such as the state tracking method have been developed to obtain faster **k**-space convergence.[14] With this method these authors studied the contributions to the Brillouin zone integral from the various **k**-space regions. However, different BZ integration techniques can give rise to very different results, even to the extent of identifying different easy axes of magnetization.

Recently, a self-consistent real-space recursion method using a tight-binding linear muffin-tin orbital (TB-LMTO) Hubbard Hamiltonian with spin-orbit coupling was implemented[15] to study the MAE of thin Fe films on a Cu(001) substrate. This study, coupled with our earlier results,[8] indicates that real-space approaches have sufficiently rapid convergence to make the task of calculating the magnetocrystalline anisotropy possible. In addition, they have the potential to make the identification of underlying mechanisms more transparent and also to allow us to investigate more complex systems.

In the past the $O(N)$ behavior of the LSMS method[6] has allowed the investigation of a number of properties of complex systems based on large $(250-1000$ atom) unit-cell models of disordered and amorphous alloys. These include the calculation of the energies of random and short-range ordered $\mathrm{Cu}_{(1-c)}\mathrm{Zn}_c$ (Ref. 6) and Ni-rich β-phase $\mathrm{Ni}_{(1-c)}\mathrm{Al}_c$ alloys,[16,17] the study of the electronic structure and energetics of bulk amorphous metals,[18,19] investigation of the nature of screening and Coulomb correlations in random alloys,[20,21] the study of magnetic short-range order in CuNi alloys,[22] and the study of noncollinear magnetism in NiFe alloys.[23] Here we extend its range of applicability by incorporating relativistic effects that allow us to treat magnetocrystalline anisotropy.

The organization of the paper is as follows. In the next section we discuss the formalism and computational implementation of the relativistic LSMS. In Sec. III we study the convergence of our method for bulk Fe, Co, and Ni, and in Sec. IV we present our conclusions.

II. METHOD

The real-space O(N) multiple-scattering method involves self-consistent calculations in which the Poisson equation is solved for the whole system, while the quantum-mechanical quantities such as electron density, the density of states, and thereby the total energy of a system, are obtained by solving the multiple-scattering problem for a local interaction zone centered on each of the atom sites. Thus the total electron density, used in solving the Poisson equation, is given by the set of individual site densities[7,6]

$$\rho(\mathbf{r})=\sum_i \rho_M^i \sigma^i(\mathbf{r}), \tag{1}$$

where $\sigma_i(\mathbf{r})$ is the truncation function for the Voronoi polyhedron that confines atom i, and M corresponds to the size of the LIZ around site i.

To calculate ρ_M we have used the real-space relativistic spin-polarized scattering theory approach. The multiple-scattering formula for the relativistic Green function $G(\mathbf{r},\mathbf{r}',E)$ has been discussed by Strange *et al.*[25,26] In the vicinity of site i it can be written as

$$G(\mathbf{r},\mathbf{r}',E)=\sum_{\Lambda,\Lambda'} Z^i_\Lambda(\mathbf{r}_i,E)[\tau_M([\zeta]_i,E)]^{i,i}_{\Lambda,\Lambda'} Z^{i\times}_{\Lambda'}(\mathbf{r}'_i,E) - \sum_{\Lambda} Z^i_\Lambda(\mathbf{r}_<,E) J^{i\times}_\Lambda(\mathbf{r}_>,E), \tag{2}$$

where $\mathbf{r}_i=\mathbf{r}-\mathbf{R}_i$ and the scattering path matrix for the cluster of the size M is

$$\tau_M([\zeta]_i,E)=[T_M^{-1}-g_M]^{-1}. \tag{3}$$

Here Λ stands for the pair of relativistic quantum numbers (κ,μ), $\times$ refers to taking the complex conjugate of the complex spherical harmonic term of Z, E is the one-electron energy, and $[\zeta]_i$ denotes a configuration of the cluster surrounding the site i. The real-space structure constants matrix g_M consists of $M\times M$ matrix subblocks that are calculated with respect to site i. The cluster t matrix T_M has M nonzero blocks on the diagonal, each of which corresponds to a single-site relativistic scattering matrix t_i.[25]

Rajagopal and MacDonald and Vosko[24] have shown that the ground-state energy of relativistic many-electron systems is a functional of the ground-state four current, and that the Kohn-Sham-Dirac equations after the Gordon decomposition of the current and neglect of diamagnetic effects are

$$\{-i\hbar c\boldsymbol{\alpha}\mathbf{p}+\beta mc^2+V^{eff}[n(\mathbf{r}),\mathbf{m}(\mathbf{r})] + \beta\boldsymbol{\sigma}\mathbf{B}^{eff}[n(\mathbf{r}),\mathbf{m}(\mathbf{r})]-E\}\psi_i(\mathbf{r})=0, \tag{4}$$

$$n(\mathbf{r})=\sum \psi_i^+(\mathbf{r})\psi_i(\mathbf{r}), \tag{5}$$

$$\mathbf{m}(\mathbf{r})=\sum \psi_i^+(\mathbf{r})\beta\boldsymbol{\sigma}\psi_i(\mathbf{r}), \tag{6}$$

$$V^{eff}[n(\mathbf{r}),\mathbf{m}(\mathbf{r})]=V^{ext}(\mathbf{r})+\frac{\delta E^{xc}[n(\mathbf{r}),\mathbf{m}(\mathbf{r})]}{\delta n(\mathbf{r})} + e^2\int\frac{n(r')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{7}$$

$$\mathbf{B}^{eff}[n(\mathbf{r}),\mathbf{m}(\mathbf{r})]=(e\hbar/2mc)\left(\mathbf{B}^{ext}+\frac{\delta E^{xc}[n(\mathbf{r}),\mathbf{m}(\mathbf{r})]}{\delta\mathbf{m}(\mathbf{r})}\right). \tag{8}$$

Here $\psi_i(\mathbf{r})$ is a four-component one-electron Dirac spinor, V^{eff} is an effective potential that is the sum of three terms: an external potential V^{ext} due to atomic nuclei, the relativistic exchange-correlation potential, and the electrostatic potential. The matrices $\boldsymbol{\alpha}$ and β are the standard Dirac matrices; $\boldsymbol{\sigma}$ is the 4×4 Pauli matrix vector; $\mathbf{B}^{eff}$ is an effective magnetic field consisting of an external magnetic field and an exchange correlation term that couples to the spin of the electron only. The functions Z^i_Λ and J^i_Λ of Eq. (2) are, respectively, properly normalized regular and irregular scattering solutions of the single-site Dirac equation corresponding to an incident wave in the Λ channel for the potential centered at the site i. For spin-dependent muffin-tin potentials, the spinor wave function Z_Λ as well as single-site t matrix have a complicated structure of the form $Z_\Lambda = \Sigma_{\Lambda'} Z_{\Lambda,\Lambda'}$, where the contributions $Z_{\Lambda,\Lambda'}$ satisfy a set of coupled, single-site Dirac equations. However, in almost all cases it is sufficient to retain only two terms, i.e., $Z_{\kappa,\mu} \cong Z_{\kappa,\mu;\kappa,\mu} + Z_{-\kappa-1,\mu;\kappa,\mu}$.[25,26]

Once we have found the Green function [Eq. (2)] we can calculate such quantities as the density of states

$$n(E) = \frac{-1}{\pi} \mathrm{Im} \int \mathrm{Tr}\ G(\mathbf{r},\mathbf{r},E) d^3r, \tag{9}$$

spin magnetic moment

$$\mathbf{m}_{spin} = \frac{-\mu_B}{\pi} \mathrm{Im} \int d^3r \int^{E_F} \mathrm{Tr}\ \beta \boldsymbol{\sigma} G(\mathbf{r},\mathbf{r},E) dE, \tag{10}$$

and orbital magnetic moment

$$\mathbf{m}_{orb} = \frac{-\mu_B}{\pi} \mathrm{Im} \int d^3r \int^{E_F} \mathrm{Tr}\ \beta \mathbf{L} G(\mathbf{r},\mathbf{r},E) dE, \tag{11}$$

where the trace is over spin space and $\mathbf{L}$ is the orbital moment operator. The charge density, which is needed to perform self-consistent calculations, is defined as

$$\rho(\mathbf{r}) = \frac{-1}{\pi} \mathrm{Im} \int^{E_F} \mathrm{Tr}\ G(\mathbf{r},\mathbf{r},E) dE. \tag{12}$$

The total energy then has been calculated as

$$E_{tot} = \sum_i^{occ} \epsilon_i - \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r-r'|} d^3r d^3r' + E_{xc}[\rho_\uparrow, \rho_\downarrow] - \sum_\sigma \int V_{xc,\sigma}(\mathbf{r}) \rho_\sigma(\mathbf{r}) d^3r, \tag{13}$$

where $\rho = \rho_\uparrow + \rho_\downarrow$ and we have used a nonrelativistic form of the exchange-correlation potential $V_{xc,\sigma}$, where the total spin-up and spin-down potentials V_σ are related to the V^{eff} and B^{eff} potential terms occurring in the Dirac equation via

$$V^{eff}(\mathbf{r}) = \frac{(V_\uparrow + V_\downarrow)}{2}, \tag{14}$$

$$B^{eff}(\mathbf{r}) = \frac{(V_\uparrow - V_\downarrow)}{2}. \tag{15}$$

Due to the variational character of the expression for the total energy in density-functional theory, the main contribution to the change in the total energy upon rotation of the magnetization direction comes from the change in the sums over the occupied single-particle energies

$$\Delta E(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \sum_i^{occ} \epsilon(\hat{\mathbf{n}})_i - \sum_i^{occ} \epsilon(\hat{\mathbf{n}}')_i, \tag{16}$$

where $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}'$ are arbitrary magnetization directions. This is the essence of the force theorem and gives a formal justification for calculating MAE as a difference between single-particle eigenvalue sums. It has been noticed by Daalderop and co-workers[3] that subtractions of two total energies, determined from two self-consistent calculations, but using spherically symmetric charge densities in the total-density calculation, will not necessarily give a more accurate answer than the force theorem. We have calculated the Fermi energy for every magnetization direction $\hat{\mathbf{n}}$, since the procedure of assuming common Fermi energies for all magnetization directions is not always justified.[3]

Since the values of MAE for bulk metals are extremely small, being of the order of several μeV, we are interested in a method that would allow one to get the necessary accuracy with the least effort. Almost all calculations of the MAE for bulk materials that we are aware of have been carried out by using **k**-space band-structure methods, in which a lot of attention must be given to the BZ integration, in particular to the partitioning of the BZ. The main difficulty of this approach is that this integration is very slowly convergent. For example, as it has been shown in Ref. 4, a converged single-particle sum to the accuracy required for the calculation of the MAE of Ni and Fe requires use of several millions of **k** points. To avoid the use of such a huge number of **k** points, schemes for interpolation of the BZ integral have been developed. The state tracking procedure introduced in Ref. 14 uses the information about the changes of the band structure with increase of the spin-orbit interaction to do such interpolation. However the accuracy of this method is not always clear.[14]

In the real-space approach we avoid BZ integration and thus are able to calculate the MAE for any possible direction of magnetization. Construction of the scattering matrix[7] at each site requires an inversion of a matrix whose size is $(l_{max}+1)^2 \times M$, where M is the size of the cluster included in the LIZ. There are several possibilities to reduce the computational effort needed to invert such a matrix. One possibility is to reduce the maximum value of the on-site angular momentum cutoff l_{max} as we go further out in real space, so that the total size of the matrix is reduced. As has been shown in many cases, it suffices to put $l_{max}=3$ on the first two shells of the cluster, cutting l_{max} to 2 or less for the rest of the LIZ.[7] In all our calculations we have put $l_{max}=3$ on the first three shells, while for the rest of the cluster $l_{max}=2$ has been used. Furthermore, due to the symmetry properties of periodic systems, the scattering matrix becomes rather sparse, so that taking this into account by using a special package designed for linear algebra calculations of sparse matrices, we can further reduce the computational effort. Combining these we speed up the calculations by a factor of 2 for the hcp Co calculations with a local interaction zone containing 81 atoms.

It is crucial for the method that the convergence of the total energy with respect to the size of the LIZ is sufficiently fast to make the calculation feasible.[8,7] As it has been shown,[7] four shells of scatteres, corresponding to $M=55$, results in an error of less than 1 mRy in case of fcc Cu. However the question remains as to how far we should go to get a convergence within the value of the MAE of bulk metals, i.e., μeV. Fortunately, it does not seem to be important to get such a good convergence in the absolute value of the total energy to obtain reasonable results for the MAE. This is because the MAE is determined as an energy difference, so that we have to check the convergence of eigenvalue sum difference for a particular LIZ. This we discuss in the next section.

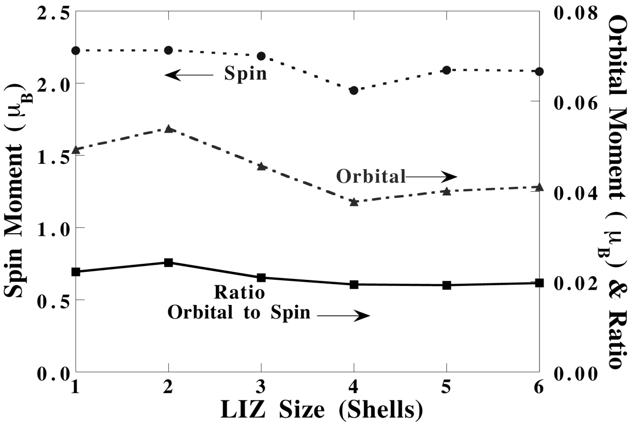

FIG. 1. Convergence of the spin and orbital magnetic moments and the ratio of orbital to spin moments as a function of the LIZ size for BCC Fe (lattice spacing: 5.27 Bohr).

III. RESULTS AND DISCUSSION

In Fig. 1 we show for Fe the convergence of the spin moment, orbital moment, and the ratio of the orbital to spin moments as a function of the LIZ size. We note that for the spin moment the value obtained with a LIZ of only one shell (13 atoms) is within 7% of the value for six shells (65 atoms). Therefore, only slight improvement is obtained by including up to five additional shells. For the orbital moment, the one shell result differs from the six shells result by 20%, while the five shells (59 atoms) result is within 2% of the result for six shells. Clearly, the spin and orbital moments have different convergence properties, the orbital moment being more sensitive to the environment. For the case of the ratio of the orbital to spin moments, the one shell result differs from the six shells result by 12%. Furthermore, the five and six shells results are essentially identical, implying that the ratio is well converged after six shells.

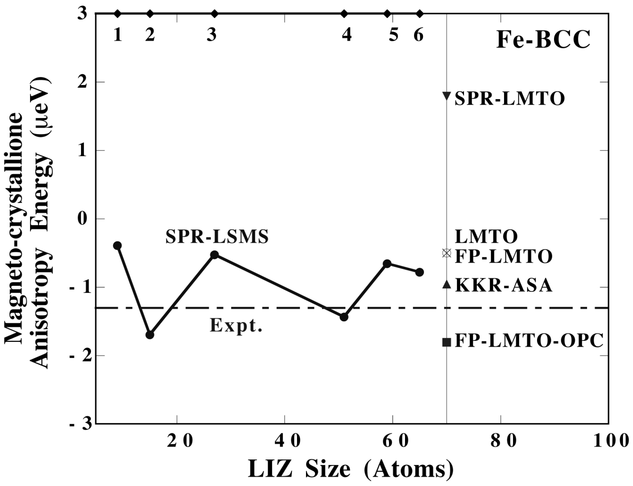

FIG. 2. Convergence of the magnetocrystalline anisotropy energy as a function of the LIZ size for BCC Fe (lattice spacing: 5.27 Bohr). Results of previous calculations SPR-LMTO (Ref. 27), LMTO (Ref. 28), FP-LMTO (Ref. 11), FP-LMTO-OPC (Ref. 11), KKR-ASA (Ref. 34) are marked on the right-hand side of the figure. Experiment is indicated by the dot-dash line.

In Table I we show our results for the spin and orbital moments together with literature values obtained using **k**-space methods and together with experimental values. One can see that our values of $2.08\mu_B$ and $0.041\mu_B$ for spin and orbital moments, respectively, compare very well with the **k**-space results. Indeed, our results are in excellent agreement with the **k**-space equivalent of our method, namely, the spin-polarized relativistic Korringa, Kohn, and Rostoker (SPR-KKR) method, for which the corresponding values are $2.08\mu_B$ and $0.056\mu_B$.[31]

TABLE I. Spin and orbital moments of BCC Fe. The experimental data stem from magnetomechanical (Ref. 32) and magnetic circular x-ray dichroism (MCXD) (Ref. 33) measurements.

$m_s(\mu_B)$	$m_o(\mu_B)$	Method	Reference
2.16	0.048	LMTO	9
2.21	0.053	SPR-LMTO	27
2.19	0.059	LMTO	28
2.19	0.091	LMTO+OPC	
2.19	0.049	FP-LMTO	11
2.19	0.078	FP-LMTO+OPC	
2.16	0.050	FLAPW	30
2.08	0.056	SPR-KKR	31
2.08	0.041	SPR-LSMS	This work
2.08	0.092	Expt.	32
2.02	0.087	Expt.	33

The magnetocrystalline anisotropy results from the total-energy difference between the easy and hard magnetization axes. For bulk transition metal magnets Fe, Co, and Ni it is very small and, consequently, difficult to calculate using the **k**-space methods. As can be seen from the results of previous calculations displayed in Fig. 2, it is possible to obtain widely different values for this quantity even within different implementations of the same band-structure method, sometimes to the point of obtaining the wrong sign. Since, the anisotropy energy is only of the order of μeV's, one might presume such a quantity to be beyond the scope of the accuracy of the real-space methodology used in this paper, where, for six shells, the absolute convergence of the total energy is only ~1 mRy. However, if the truncation errors affect the

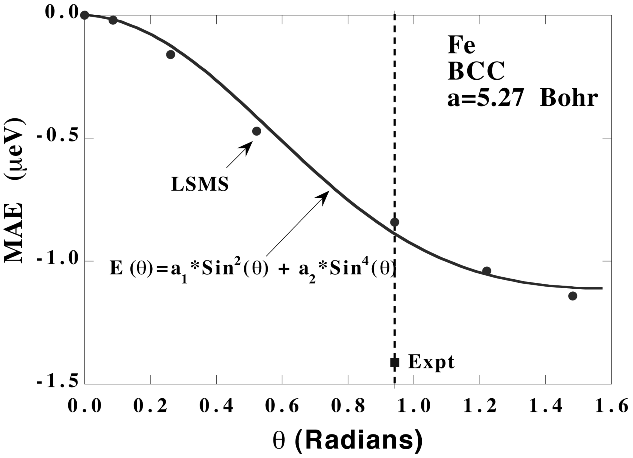

FIG. 3. Angular dependence of MAE in BCC Fe. Full circles are the seven calculated values. The full line is a least-squares fit through these points.

TABLE II. Magnetocrystalline anisotropy energy, spin and orbital moments of FCC Ni.

This work shells	m$_s(\mu_B)$	m$_o(\mu_B)$	E(001)-E(111) [μeV]
4	0.51 970	0.0367	0.408
6	0.59 582	0.0463	-0.544
7	0.54 558	0.0444	-0.434
Method	m$_s(\mu_B)$	m$_o(\mu_B)$	E(001)-E(111) [μeV]
SPR-LMTO (Ref. 9)	0.59 800	0.044	-0.500
SPR-LMTO (Ref. 10)	0.601 00	0.051	-2.700
SPR-KKR (Ref. 34)			0.110
FP-LMTO (Ref. 11)	0.6085	0.0457	-0.5
FP-LMTO+OPC (Ref. 11)	0.6109	0.0655	0.5
Expt. (Ref. 35)	0.57 000	0.05	2.700

easy and hard axis energies in the same way, it may still be possible to obtain a reliable anisotropy energy. As we shall see now, this appears to be the case, suggesting that origins of the magnetocrystalline anisotropy are relatively local in real space.

We have calculated $\Delta E([001],[111])$ for LIZ sizes from one to six shells. For each LIZ size we converge the one-electron term to an accuracy of 10^{-9} Ry. Our results are shown in Fig. 2 together with the results of previous calculations using conventional **k**-space methods. We note that an attempt to calculate $\Delta E([001],[111])$ by means of the **k**-space equivalent of our method, namely, the SPR-KKR band-structure method, with a non-self-consistent potential, yielded an unrealistic value of $+45.0$ μeV.[12] However, in another SPR-KKR calculation[34] with common Fermi energies and within the atomic sphere approximation yielded a value of -0.95 μeV, very close to our result of -0.78 μeV. Noteworthy is that, in our calculation, the sign, one of the major sources of contention between the various **k**-space calculations, is independent of the number of shells up to six shells.

The power of the real-space approach is illustrated in Fig. 3 where we plot the MAE as a function of angle θ between the magnetization direction and the z axis ([001]). These calculations were done for a LIZ of 5 shells or 59 atoms, with angular momentum cutoffs of $l_{max}=4$ on the central atom, $l_{max}=3$ on the first three shells, and $l_{max}=2$ on the final two shells of the LIZ. Such a LIZ, we showed above, converged the MAE between the [001] and [111] directions. We compare our *ab initio* values with a phenomenological expression $E(\theta)=K_1[\sin^2\theta-(0.75-K_2/K_1)\sin^4\theta]+O(\sin^6\theta)$.[13] From the least-squares fit of our seven *ab initio* calculated values we evaluate K_2/K_1 to be around 0.35, which is in reasonable agreement with experimental values around 0.1.[13] This demonstrates that our method has the possibility to determine the ratio of the anisotropy constants K_1 and K_2.

For Ni, Table II, we find that we need at least four shells of atoms to obtain a magnetic moment. The values of orbital and magnetic moments at the fourth shell are reasonably close to the values for the six and seven shell calculations. We observe again that different calculations give different signs for the value of MAE. In our calculations the sign of the MAE changes as we increase the LIZ from four shells to six shells. This contrasts with the results on bcc Fe and fcc Co where no sign change occurs as a function of LIZ. However, further increasing the LIZ to seven shells does not change the sign anymore. While this cannot be construed as converged, it is satisfactory to see agreement with the SPR-LMTO calculations.[3,11] Comparing our results with the **k**-space equivalent of our method, SPR-KKR,[34] we note that in comparison to the Fe calculations the agreement is less satisfactory.

For fcc Co (see Table III) we find fast convergence of the spin and orbital moments and the MAE. This situation is reminiscent of the Fe results of Fig. 1. The orbital and spin

TABLE III. Magnetocrystalline anisotropy energy, spin, and orbital moments of FCC Co.

This work shells	m$_s(\mu_B)$	m$_o(\mu_B)$	E(001)-E(111) [μeV]
1 [13]	1.4160	0.0725	1.100
4 [55]	1.5812	0.0741	0.950
6 [87]	1.5900	0.0740	1.050
Method	m$_s(\mu_B)$	m$_o(\mu_B)$	E(001)-E(111) [μeV]
SPR-LMTO (Ref. 10)	1.594	0.073	
FP-LMTO (Ref. 11)	1.6184	0.0745	0.5
FP-LMTO+OPC (Ref. 11)	1.6187	0.1180	2.2
SPR-KKR (Ref. 34)			0.86
Experiment (Ref. 36)			1.300

TABLE IV. Magnetocrystalline anisotropy energy, spin, and orbital moments of HCP Co.

This work shells	$m_s(\mu_B)$	$m_o(\mu_B)$	E(0001)-E(1010) [μeV]
2 [13]	1.496	0.074	-10.8
3 [19]	1.586	0.077	12.1
5 [33]	1.708	0.065	123.7
6 [39]	1.686	0.066	-106.0
7 [51]	1.643	0.069	63.2
10 [81]	1.572	0.082	-100.0
Method	$m_s(\mu_B)$	$m_o(\mu_B)$	E(0001)-E(1010) [μeV]
SPR-LMTO (Ref. 9)			
spd	1.6100	0.085	-29
spdf	1.5700	0.079	16
Expt. (Ref. 36)	1.5900	0.16	-65

moments are converged to 0.5% and 0.1%, respectively, after 4 shells. The result for the MAE is most interesting. Its value of 1.050 μeV is comparable to the result of 0.86 μeV obtained with the SPR-KKR,[34] however it is twice as big as the FP-LMTO result of 0.5 μeV. The present result comes within 20% of the experimentally deduced value of 1.3, suggesting that in the case of Co the inclusion of orbital polarization correction[11] might not be necessary.

Surprisingly, we find for hcp Co a much slower convergence of spin and orbital moment than encountered in any of our previous calculations for bcc Fe, fcc Ni, and fcc Co. For instance, the spin moment is only converged up to 4.5% when comparing the results of 51 atoms with 81 atoms. It is worse for the orbital moment where the same comparison gives only a convergence of 16%. It should therefore come as no surprise that we did not manage to converge the MAE. Sign changes occur frequently and still occur between 51 and 81 atoms. These results might be a consequence of the reduced symmetry since hcp has a lower symmetry than the fcc and bcc structures that we previously studied. Moreover, our calculations were performed for the experimental c/a ratio that is 0.7% smaller than the ideal c/a ratio. This further reduced the symmetry. Another possible source of convergence problems might be associated with the angular momentum cutoff. A SPR-LMTO (Ref. 9) (Table IV) shows that the spin and orbital moments still change substantially on going from $l_{max}=2$ to $l_{max}=3$ and the MAE even changes sign. In our calculations we use $l_{max}=3$ up 33 atoms and beyond this $l_{max}=2$ that we found to be sufficiently convergent.

IV. CONCLUSIONS

In summary, we have presented a real-space approach for performing relativistic spin-polarized electronic structure calculations. We have used the method to calculate the spin and orbital magnetic moments of Fe, Ni, and Co. These quantities appear to be sufficiently rapidly convergent to make their calculation in real space tractable. In addition, we have calculated the magnetocrystalline anisotropy energy. We have found that if the spin and orbital moments converged rapidly, so did the MAE. This was the case for bcc Fe and fcc Co. For fcc Ni it took 55 atoms to build up a magnetic moment and we needed a bigger number of atoms to converge the spin and orbital moments and the MAE. Cobalt in the hcp structure was the worst case we have studied so far, and for 81 atoms neither the spin and orbital moments nor the MAE are converged.

In case of hcp Co, the magnetic anisotropy is considerably larger than in cubic systems, because of reduced symmetry. Thus one might expect that the calculations should be easier. However, as our calculations for the hcp Co show, neither the magnetic moment nor the magnetocrystalline anisotropy energy converge well for the LIZ sizes that are sufficient for systems with cubic symmetry. To understand this result and to improve the convergence, we are now implementing screened structure constants techniques.[29] These will allow us to construct the larger LIZ's needed for hcp Co and, to a lesser extent, fcc Ni. These techniques result in reasonably sparse matrices whose inverse can be calculated by specially designed sparse matrix algorithms, allowing one to deal with considerably larger clusters. The power of the real-space method lies in the possibility of considering nonperiodic systems or systems with reduced symmetries. Thus, the question of real-space convergence for such systems is crucial for the method and we will discuss it in more detail in future publications.

Our preliminary experience with the screening techniques indicates that calculations for LIZ's of several hundreds of atoms can be routinely performed on typical workstations. Since the methodology is by construction of order N, it opens up a possibility of studying spin and orbital moments and magnetocrystalline anisotropy in complex inhomogeneous systems such as magnetic multilayers with interface roughness and disordered alloys.

ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences, Division of Materials Science (GMS) and Mathematical, Information, and Computational Sciences Division (GMS, YW, DMN, and WAS), US-DOE, under subcontract No. DEAC05-84OR21400 with Lockheed-Martin Energy Systems, Inc. The Work of S.V.B. was supported by EPSRC GR/K09793.

---

[1] F. E. Luborsky, J. D. Livingston, and G. Y. Chin, in *Physical Metallurgy*, edited by R. W. Cahn and P. Haasen (North-Holland, Amsterdam, 1983).

[2] J. G. Gay and R. Richter, Phys. Rev. Lett. **56**, 2728 (1986).

[3] G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, Phys. Rev. B **44**, 12 054 (1992).

[4] G. Y. Guo, W. M. Temmerman, and H. Ebert, J. Phys.: Condens. Matter **3**, 8205 (1991).

[5] M. B. Suvasini, G. Y. Guo, W. M. Temmerman, and G. A. Gehring, Phys. Rev. Lett. **71**, 2983 (1993).

[6] Yang Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson, Z. Szotek, and W. M. Temmerman, Phys. Rev. Lett. **75**, 2867 (1995).

[7] D. M. C. Nicholson, G. M. Stocks, Y. Wang, W. A. Shelton, Z. Szotek, and W. M. Temmerman, Phys. Rev. B **50**, 14 686 (1994).

[8] S. V. Beiden, G. Y. Guo, W. M. Temmerman, Z. Szotek, G. A. Gehring, Yang Wang, G. M. Stocks, D. M. C. Nicholson, W. A. Shelton, and H. Ebert, in *Materials Theory, Simulations, and Parallel Algorithms*, edited by E. Kaxiras, J. Joannopoulos, P. Vashista, and R. K. Kalia, MRS Symposia Proceedings No. 408 (Materials Research Society, Pittsburgh, 1996), p. 73.

[9] G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, Phys. Rev. B **41**, 11 919 (1990).

[10] G. Y. Guo, W. M. Temmerman, and H. Ebert, Physica B **172**, 61 (1991).

[11] J. Trygg, B. Johansson, O. Eriksson, and J. M. Wills, Phys. Rev. Lett. **75**, 2871 (1995).

[12] G. Hoermandinger and P. Weinberger, J. Phys.: Condens. Matter **4**, 2185 (1992).

[13] *Ferromagnetic Materials. Vol. 1*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980).

[14] D. S. Wang, R. Wu, and A. J. Freeman, Phys. Rev. Lett. **70**, 869 (1993).

[15] R. Lorenz and J. Hafner, Phys. Rev. B **54**, 15 937 (1996).

[16] Yang Wang, G. M. Stocks, D. M. C. Nicholson, W. A. Shelton, E. L. Hines, Z. Szotek, and W. M. Temmerman, in *High-Temperature Ordered Intermetallic Alloys VI*, edited by J. A. Horton, I. Baker, S. Hanada, R. D. Noebe, and D. S. Schwartz, MRS Symposia Proceedings No. 364 (Materials Research Society, Pittsburgh, 1995), p. 381.

[17] G. A. Botton, G. Y. Guo, W. M. Temmerman, Z. Szotek, C. J. Humphreys, Yang Wang, G. M. Stocks, D. M. C. Nicholson, and W. A. Shelton, in *Materials Theory, Simulations, and Parallel Algorithms* (Ref. 8), p. 567.

[18] J. C. Swihart, D. M. C. Nicholson, G. M. Stocks, Y. Wang, W. A. Shelton, and H. Yang, J. Non-Cryst. Solids **205-207**, 841 (1996).

[19] D. M. C. Nicholson, G. M. Stocks, W. A. Shelton, Y. Wang, and J. C. Swihart, Metall. Mater. Trans. (to be published).

[20] J. S. Faulkner, Yang Wang, and G. M. Stocks, Phys. Rev. B **52**, 17 106 (1995).

[21] J. S. Faulkner, Yang Wang, and G. M. Stocks, Phys. Rev. B **55**, 7492 (1997).

[22] Yang Wang, G. M. Stocks, D. M. C. Nicholson, W. A. Shelton, Z. Szotek, and W. M. Temmerman, in *Materials Theory, Simulations, and Parallel Algorithms* (Ref. 8), p. 585.

[23] G. M. Stocks, Yang Wang, D. M. C. Nicholson, W. A. Shelton, Z. Szotek, W. M. Temmerman, B. N. Harmon, and V. P. Antropov, in *Materials Theory, Simulations, and Parallel Algorithms* (Ref. 8), p. 157.

[24] A. K. Rajagopal, J. Phys. C **11**, L943 (1978); A. H. MacDonald and S. H. Vosko, *ibid.* **12**, 2977 (1979).

[25] P. Strange, H. Ebert, J. B. Staunton, and B. L. Gyorffy, J. Phys.: Condens. Matter **1**, 2959 (1991).

[26] P. Strange, J. B. Staunton, and B. L. Gyorffy, J. Phys. C **17**, 3355 (1984).

[27] G. Y. Guo, H. Ebert, W. M. Temmerman, and D. J. Durham, Phys. Rev. B **50**, 3861 (1994).

[28] P. Soderlind, O. Eriksson, B. Johansson, R. C. Albers, and A. M. Boring, Phys. Rev. B **45**, 12 911 (1992).

[29] R. Zeller, P. H. Dederichs, B. Ujfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B **52**, 8807 (1995).

[30] R. Wu, D. Wang, and A. J. Freeman, Phys. Rev. Lett. **71**, 3581 (1993).

[31] H. Ebert, P. Strange, and B. L. Gyorffy, J. Phys. F **18**, L135 (1988).

[32] M. B. Stearns, in *Magnetic Properties of 3d, 4d and 5d Elements, Alloys and Compounds*, Vol. III of *Landolt-Börnstein, New Series*, edited by K.-H. Hellewege and O. Madelung (Springer-Verlag, Berlin, 1987).

[33] C. T. Chen, Y. U. Idzerda, H.-J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette, Phys. Rev. Lett. **75**, 152 (1995).

[34] S. S. A. Razee, J. B. Staunton, and F. J. Pinski, J. Phys. Condens. Matter (to be published).

[35] P. Escudier, Ann. Phys. (Leipzig) **9**, 125 (1975); G. Aubert and B. Michelutti, Physica B **86-88**, 329 (1977); D. Bonnenberg, K. A. Hempel, and H. P. Wijn, in *Magnetic Properties of 3d, 4d and 5d Elements, Alloys and Compounds* (Ref. 32).

[36] D. Weller, G. R. Harp, R. F. C. Farrow, A. Cebollada, and J. Sticht, Phys. Rev. Lett. **72**, 2097 (1991).