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Symmetry aspects in spin-polarized relativistic electronic structure calculations based on the Green function method

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Abstract. The consideration of spin-orbit coupling in spin-polarized electronic structure calculations leads to magnetic anisotropies and reduces the symmetry of the problem. The theory of magnetic groups is required to make full use of the remaining symmetry. A systematic method is presented to treat this problem in the framework of the Green function method. An application to the magnetocrystalline anisotropy energy of Fe fails to converge numerically but reveals where this effect originates as a function of reciprocal space vector and energy.

1. Introduction

The description of magnetic phenomena in solids in the itinerant electron picture implies a spin-polarized formulation of the band structure problem. There are quite a few effects which also require the consideration of spin-orbit coupling, such as the magnetocrystalline anisotropy, orbital magnetism, and magneto-optical properties.

In general, any method of solving the electronic structure problem in periodic solids requires some way of sampling the Brillouin zone (BZ). In the absence of magnetic effects, this can be reduced by symmetry considerations to just one irreducible part of the BZ (IBZ). Taking the exchange splitting into account but ignoring the spin-orbit interaction (the semi-relativistic approximation) still permits this way of proceeding. In the relativistic scheme, spin-orbit coupling is treated implicitly from the start and only a non-spin-polarized calculation, i.e. ignoring the exchange splitting, allows one to reduce the Brillouin zone integration in that way.

Consideration of both spin-orbit coupling and exchange splitting reduces the symmetry of the problem which means that now more than one IBZ must be taken into account (see e.g. Cracknell 1970). For band structure methods like LMTO, APW or KKR this merely means that the computational effort increases but the formalism is unchanged. Essentially the same is true for the Green function method, but here greater care is required because one has to take into account the antilinear properties of some of the remaining symmetries.

In the following, we will develop a systematic way of treating the magnetic symmetry for the Green function method, along with a prescription of the set of IBZ over which one has to integrate. Certain matrix properties of the scattering path operator, a representation of the Green function, will thus become obvious. We employ a relativistic scheme but the group theoretical considerations are also valid

in a non-relativistic spin-polarized Green function formalism, where the spin-orbit coupling is treated as a perturbation. In section 3, we apply this formalism to the magnetocrystalline anisotropy energy (MAE) of BCC Fe. We locate the crucial points in its calculation both in k space and as a function of the energy. Conclusions are summarized in section 4.

2. Magnetic symmetry in the Green function method

In order to treat the effects of spin polarization in the context of relativistic density functional theory, one generally uses an effective magnetic field B^{eff} which couples to the spin only (MacDonald and Vosko 1979). This field is assumed constant in orientation but varies as a function of space. By splitting the Dirac Hamiltonian \hat{H} into a non-magnetic term \hat{H}_0 and the magnetic contribution \hat{H}_1 , \hat{H} can be written as (Strange *et al* 1984, Ebert 1988)

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_1 \\ \hat{H}_0 &= -i\hbar c\alpha\nabla + \beta mc^2 + I V^{\text{eff}}[n, m] \\ \hat{H}_1 &= \beta\sigma B^{\text{eff}}[n, m]\end{aligned}\quad (1)$$

where

$$\begin{aligned}V^{\text{eff}} &= V^{\text{ext}} + V^{\text{Hartree}} + \frac{\delta E_{\text{xc}}}{\delta n} \\ B^{\text{eff}} &= B^{\text{ext}} + \frac{e\hbar}{2mc} \frac{\delta E_{\text{xc}}}{\delta m}.\end{aligned}\quad (2)$$

Consider first the symmetry properties of the non-spin polarized case, i.e. the Hamiltonian \hat{H}_0 . We assume a crystal structure with a symmorphic space group and concentrate on the point group of the problem. Let G denote the point group of unitary operations (proper and improper rotations). The operation of time reversal, θ , also leaves \hat{H}_0 invariant. Therefore, the full symmetry point group of \hat{H}_0 , denoted by \bar{G} , is twice as large as G . It is a magnetic point group of type II, a so called grey Shubnikov group:

$$\bar{G} = G + \theta G. \quad (3)$$

If, additionally to time reversal θ , the potential is symmetric under space inversion I , we have at least twofold degeneracy everywhere in the Brillouin zone, the well known Kramers degeneracy. In the relativistic formalism employed here, this double degeneracy shows up explicitly since the number of basis functions is doubled as compared to the non-relativistic case, while the number of energy bands is the same.

Let us now inspect the magnetic term, \hat{H}_1 . The unitary operations $g \in G$, which leave the direction of the magnetic field B invariant, form a subgroup H in G . Since the time reversal θ reverts the orientation of B , anti-unitary elements θg are permissible if their unitary part g cancels this reversal. We denote by Γ the subgroup of G which preserves B up to the sign. If there is an operation in Γ which changes the sign of B , then it can only be a twofold proper or improper rotation

(a so called bilateral operation, see Altmann 1986) with an axis perpendicular to B . This particular twofold rotation, $C_{2\perp}$, does not exist in general but only for special orientations of B relative to the crystal axes. However, in the cases of B pointing in the cubic [001], [111], and [011] directions, there is at least one such $C_{2\perp}$ so we will assume its existence in the following. The point group M which leaves the complete Hamiltonian $\hat{H}_0 + \hat{H}_1$ invariant is a type III magnetic point group, a so called black-and-white Shubnikov group. It is given by

$$M = H + \theta(\Gamma - H). \quad (4)$$

Because H is a subgroup of Γ , we can decompose Γ into right cosets of H using $C_{2\perp}$ as coset representative:

$$\Gamma = H + HC_{2\perp}. \quad (5)$$

Since $G \supset \Gamma \supset H$, the unitary point group G can be decomposed into cosets in the following way:

$$G = \sum_{i=1}^{n_\Gamma} \Gamma g_i = \sum_{i=1}^{n_\Gamma} (H g_i + HC_{2\perp} g_i) \quad (6)$$

where $n_\Gamma = |G|/|\Gamma|$ and the group order of a given group A is denoted by $|A|$. The coset representatives g_i are not uniquely defined since any product γg_i with an element $\gamma \in \Gamma$ can serve as a representative of the same coset. The g_i rotate B out of its original orientation. As an illustration, some examples of these groups are shown in table 1 for the cubic case.

The quantity central to the Green function method is the site-diagonal scattering path operator $\tau(E)$ (see e.g. Faulkner and Stocks 1980). In the case of an infinite crystal, i.e. translational invariance, it is given by an integral over the Brillouin zone. We shall now make use of the above group decomposition to replace this integral by a number of integrals over irreducible parts of the Brillouin zone such that this number is as small as possible. In the following, τ denotes the site-diagonal scattering path operator, t the single-site scattering matrix, B the KKR structure constants, and D a transformation matrix. The energy argument of τ , t and B is left implicit. Then

$$\tau = \int_{BZ} d^3k \tau(k) \quad (7)$$

$$\tau(k) = [t^{-1} - i\kappa\mathbf{1} - B(k)]^{-1} \quad (8)$$

where $\kappa = \sqrt{E}$. The integral over the full Brillouin zone (BZ) can be considered as a sum over integrals over all irreducible parts of the Brillouin zone (IBZ). If IBZ_1 denotes a special IBZ, then all other IBZ can be generated from it by some proper or improper rotation $R \in G$. Denoting these IBZ by IBZ_R , we have

$$IBZ_R = \{Rk \mid k \in IBZ_1\} \quad R \in G. \quad (9)$$

Using the transformation properties of the structure constants (see appendix 3),

$$B(Rk) = D(R) B(k) D(R^{-1}) \quad (10)$$

Table 1. Symmetry groups for some orientations of the effective magnetic field in a cubic system where the group G is the cubic group $m\bar{3}m(O_h)$. \tilde{B} is the orientation of the B field. For H, M, Γ and $C_{2\perp}$ see text. \tilde{R} means multiplication of R by the inversion I , \underline{R} means multiplication by the time reversal θ .

\tilde{B}	H			M			Γ				
	Int.	Schönflies	$ H $	H	Int.	Shubnikov	$ M $	M	$C_{2\perp}$	Int.	Schönflies
001 (z)	$4/m$	C_{4h}	8	E 4_x^\pm 2_x I 4_x^\pm 2_x	$4/m\bar{m}m$	$m \cdot 4 : m$	16	E I 2_x 2_x 4_x^\pm 4_x^\pm 2_x 2_y 2_a 2_b 2_x 2_y 2_a 2_b	2_x 2_y 2_a 2_b	$4/m\bar{m}m$	D_{4h}
111 (l)	$\bar{3}$	$C_{3i}(S_6)$	6	E 3_1^\pm 3_1^\pm	$\bar{3}m$	$\bar{6} \cdot m$	12	E I 3_1^\pm 3_1^\pm 2_b 2_c 2_f 2_b 2_c 2_f	2_b 2_c 2_f	$\bar{3}m$	D_{3d}
011 (d)	$2/m$	C_{2h}	4	E 2_d I 2_d	$m\bar{m}m$	$m \cdot 2 : m$	8	E I 2_d 2_d 2_x 2_f 2_x 2_f	2_x 2_f	$m\bar{m}m$	$D_{2h}(V_h)$

the integral over IBZ_R is given by

$$Q_R = D(R) \int_{\text{IBZ}_1} d^3k [D(R^{-1}) t^{-1} D(R) - i\kappa\mathbf{1} - B(\mathbf{k})]^{-1} D(R^{-1}). \quad (11)$$

In the non-magnetic case, the single-site scattering problem is symmetric under all $R \in G$ and therefore Q_R is nothing but $D(R) Q_E D(R^{-1})$, where E refers to the identity element in G . Summing over all $R \in G$ leads to a matrix structure of τ which reflects the point group symmetry G (Weinberger 1990).

In the magnetic case, the t matrix depends on the orientation of B and is invariant only under the elements of the magnetic group M defined in equation (4), half of which are anti-unitary. However, because of the need to transform the IBZ only with unitary elements $R \in G$, we will use the unitary group Γ rather than M to reduce the Brillouin zone integral in (7). Only then we will make use of the close relationship between Γ and M to replace the effect of $C_{2\perp}$ by that of θ , thus introducing anti-unitary elements as well. (This complication does not arise in the band structure methods mentioned in the introduction, because constant energy surfaces, considered as three-dimensional objects, have the unitary point symmetry Γ rather than M . The energy eigenvalues themselves are given in general by the zero of some determinant, and all that the time reversal does to the corresponding matrix is essentially replacing it by its transpose. This has no influence on the position of the energy band so one can get off without explicit consideration of θ).

Consider first those elements $R \in G$ which can be written as $R = hg_i$, $h \in H$ (see equation (6)). From equation (11) it follows that

$$Q_R = D(h) Q_{g_i} D(h^{-1}) \quad (12)$$

i.e. for each coset representative g_i there are $|H|$ IBZ, the integrals over which are related by transformations with elements of H . The integral Q_{g_i} has to be evaluated numerically for each coset Γg_i in G .

Next, we consider those elements $R \in G$ which can be written as $R = hC_{2\perp}g_i$. Equation (11) gives

$$Q_R = D(hC_{2\perp}g_i) \int_{\text{IBZ}_1} d^3k [D(g_i^{-1}C_{2\perp}^{-1}) t^{-1} D(C_{2\perp}g_i) - i\kappa\mathbf{1} - B(\mathbf{k})]^{-1} \times D(g_i^{-1}C_{2\perp}^{-1}h^{-1}). \quad (13)$$

Since $C_{2\perp}\theta$ is a symmetry operation of the Hamiltonian, we can replace the twofold rotation of t^{-1} by a time reversal transformation according to equation (A9) in appendix 1. The structure constants $B(\mathbf{k})$ are Hermitean and invariant under the combined operation of time reversal θ and inversion I †

$$B(\mathbf{k}) = D((\theta I)^{-1}) B^*(\mathbf{k}) D^*(\theta I) \quad (14)$$

Both the Hermitean property and equation (14) are restricted to real values of the energy; their combination, however,

$$B(\mathbf{k}) = D((\theta I)^{-1}) B^T(\mathbf{k}) D^*(\theta I) \quad (15)$$

† See e.g. Holzwarth (1974) who gives the same expression but without a matrix notation.

is also valid in the complex energy plane (here we used $D^*(\theta^{-1}) = D^+(\theta)$; the superscript T denotes transposed matrices). In terms of equation (A9) in appendix 1 for the t matrix, and using the fact that θ commutes with all point group operations, equation (13) can be written as

$$Q_R = D(h) D(C_i) Q_{g_i}^T D^*(C_i^{-1}) D(h^{-1}) \quad (16)$$

where the operation C_i is defined as

$$C_{2\perp} \theta^{-1} I. \quad (17)$$

In obtaining (16), we have also assumed invariance of t under space inversion I . Care must be taken to obey the multiplication rules of the magnetic co-representations (see appendix 2). Note that the integral Q_{g_i} is the same as in equation (12) which means that no additional numerical work is required. Similar to the non-magnetic case, we can express the BZ integral as a sum over group operations. Our irreducible part of the Brillouin zone now consists of the IBZ_{g_i} for all cosets i of the group Γ in G . Since there is some freedom in choosing the coset representatives, the choice of the IBZ_{g_i} is not unique. Let us denote the integral over this enlarged IBZ by \bar{Q} :

$$\bar{Q} = \sum_{i=1}^{n_\Gamma} Q_{g_i}. \quad (18)$$

It is this quantity which has to be computed numerically. The total BZ integral is then given by

$$\tau = \sum_{h \in H} D(h) [\bar{Q} + D(C_i) \bar{Q}^T D^*(C_i^{-1})] D(h^{-1}) \quad (19)$$

$$= \sum_{h \in H} D(h) \bar{Q} D(h^{-1}) + D(C_i) \left[\sum_{h \in H} D(h) \bar{Q} D(h^{-1}) \right]^T D^*(C_i^{-1}). \quad (20)$$

The last step (interchanging the h and C_i) is possible because H is a subgroup of index 2 in Γ and therefore a normal subgroup, and $C_{2\perp}$ is an element of Γ . For a normal subgroup, all left cosets coincide with the corresponding right cosets, thus the sum over transformations $hC_{2\perp}$ is identical to the sum over $C_{2\perp}h$.

With equation (20) we have arrived at a formulation which requires only $n_\Gamma = |G|/|\Gamma|$ numerical integrations. This is the same as in the band structure methods, as it should be since the symmetry group M is of the same order as the unitary group Γ . Moreover, the explicit form of the expressions permits us to investigate the matrix properties of τ for certain orientations of the magnetic field. Consider the case of B_{eff} pointing in the z direction. If we choose $C_{2\perp}$ to be C_{2y} , the transformation matrix $D(C_i)$ (see appendix 2, equation A24) becomes $-i$ times the unit matrix and τ is seen to be explicitly symmetrized. There seems to be an inconsistency because if we choose $C_{2\perp}$ to be C_{2x} instead of C_{2y} , or C_{2a} or C_{2b} , the matrix $D(C_i)$ is no longer proportional to the unit matrix, but involves a phase factor $\phi_{\mu\mu'}$ for each element $(\kappa\mu, \kappa'\mu')$ of the transformed matrix (see table 2). However, since in this particular case the matrix structure of τ is such that only matrix elements with

$\mu' = \mu$, $\mu' = \mu \pm 4$ are non-zero (Strange *et al* 1989a), the phase factor $\phi_{\mu\mu'}$ for these elements is always unity. This has to be compared to a magnetic field pointing in the [111] direction. The only $C_{2\perp}$ perpendicular to the z axis† is C_{2b} . There are now several elements non-zero with $(\mu - \mu') \bmod 4 \neq 0$, so the phase factors $\phi_{\mu\mu'}$ are different from unity and τ is no longer a symmetric matrix. Similar arguments apply to the [011] case, where we have to use C_{2x} . This behaviour is similar to that of the single-site t matrix (see appendix 1).

Table 2. The phase factors $\phi_{\mu\mu'}$ which arise if a matrix is transformed with $D(C_i)$, where $C_i = C_{2\perp} \theta^{-1} I$ and $C_{2\perp}$ is perpendicular to the z axis. $\mu - \mu'$ is of modulo 4.

$C_{2\perp}$	$\mu - \mu' = 0$	1	2	3
C_{2x}	1	-1	1	-1
C_{2y}	1	1	1	1
C_{2a}	1	i	-1	-i
C_{2b}	1	-i	-1	i

3. The magnetocrystalline anisotropy energy of Fe

The problem of magnetocrystalline anisotropy has been treated extensively in the past. Quite recently, there were a few attempts to calculate the anisotropy energy of the magnetic elements Fe, Co and Ni from first principles (Fritsche *et al* 1987, Strange *et al* 1989b, Daalderop *et al* 1990, Guo *et al* 1991).

The anisotropy energy is given as the difference of the total energies corresponding to different orientations n of the magnetization. It is a common approach in density functional theory to make use of the so called force theorem and thus to replace the difference of total energies by the difference of the eigenvalue sums. Using the density of states (DOS) $n_n(E)$ for a given n vector, the magnetocrystalline anisotropy energy (MAE) is given by

$$\Delta E^{n-n'} = \int^{E_F[n]} dE E n_n(E) - \int^{E_F[n']} dE E n_{n'}(E). \quad (21)$$

In the framework of multiple scattering theory, the DOS is given in terms of the scattering path operator $\tau(E)$ discussed in the previous section:

$$\begin{aligned} n(E) &= -\frac{1}{\pi} \text{Im} \int d^3r \text{tr} G(r, r, E) \\ &= -\frac{1}{\pi} \text{Im} \left(\sum_{KK'} \int d^3r Z_{K'}^+(r) Z_K(r) \tau_{KK'}(E) - \sum_K J_K^+(r) Z_K(r) \right) \end{aligned} \quad (22)$$

$$(23)$$

where the Z and J are scattering solutions at energy E which at the origin are regular and irregular, respectively (see Faulkner (1979) for the non-relativistic case,

† Of course, the restriction of $C_{2\perp}$ to lie in the xy plane is entirely a matter of convenience in order to have a simple form for the rotation matrix.

Schadler *et al* (1987) or Strange *et al* (1989a) for the relativistic case). The scattering path operator is evaluated at complex energies to smear out the integrand in k space. Thus, the energy integrations over $n(E)$ and $En(E)$, required to determine the Fermi energy and the eigenvalue sum, are replaced by contour integrations in the complex plane. Here, the second term in equation (23) is no longer purely real, as it is on the real axis, and must be taken into account. However, one can avoid its calculation by splitting the Green function into single-site-scattering and back-scattering parts (see e.g. Pinski and Stocks 1985, Akai 1989):

$$G = G^s + G^b \quad (24)$$

$$G^s(\mathbf{r}, \mathbf{r}', E) = \sum_{KK'} Z_K(\mathbf{r}) t_{KK'}(E) Z_{K'}^+(\mathbf{r}') - \sum_K Z_K(\mathbf{r}) J_K^+(\mathbf{r}')$$

$$G^b(\mathbf{r}, \mathbf{r}', E) = \sum_{KK'} Z_K(\mathbf{r}) [\tau_{KK'}(E) - t_{KK'}(E)] Z_{K'}^+(\mathbf{r}'). \quad (25)$$

G^s does not require any Brillouin zone integration and can readily be calculated for real energies, where the second term of Equation (25) is real and does not contribute to the density of states. The part G^b has to be evaluated for complex values of the energy, where the integrand of the Brillouin zone integral equation (7) is smeared out. Thus, the energy integrals of equation (21) for the eigenvalue sums and similar ones for the determination of the Fermi energy are split into an integral along the real axis with an integrand corresponding to equation (25), and a contour integral with an integrand corresponding to equation (26). We chose a rectangular contour starting below the bottom of the valence band.

Strange *et al* (1989a) have described how to find the Fermi energy by returning close to the real axis at an estimated value of E_F , calculating $\tau(E)$ at a few points parallel to the real axis and obtaining the last part of the contour by analytic continuation from these points. In our calculation, the imaginary part of the contour was only about 6 mRyd (0.004 dimensionless units), so the short vertical part of the contour was determined by analytic continuation from the horizontal part, using a back-folding technique of Eschrig *et al* (1986). The Fermi energies, and thus the rectangular contours, for the two magnetizations were determined separately.

The potential used in this calculation is the spin-polarized potential of BCC Fe by Moruzzi *et al* (1978). The computational effort involved in this kind of calculation prevents us from iterating the potential to self-consistency. An illustration of the influence of spin-orbit coupling is given in figure 1, where the energy bands along the coordinate axis (ΓH) show differences up to 0.1 eV as a function of the relative angle to the magnetization. This is remarkably much bigger than the MAE which experimentally is found to be $-1.4 \mu\text{eV}$. In figure 2 some of these energy differences are shown in more detail. The region in k space with the most pronounced band deformations and thus contributions to the MAE is found to be on the k coordinate axes at about $0.7 k_H$, where k_H is the reciprocal vector pointing from Γ to H , and somewhat less in the coordinate planes around these regions. Figure 2(b) shows the correct degeneracies: with a magnetization pointing along the z axis, the two axes perpendicular to it are degenerate to each other but different from the k_z axis. With a magnetization in the $[111]$ direction, all the coordinate axes in k space are degenerate.

The BZ integral equation (7) was performed using the method of special directions (Fehlner and Vosko 1976) and the closely related prism method (Stocks *et al* 1979).

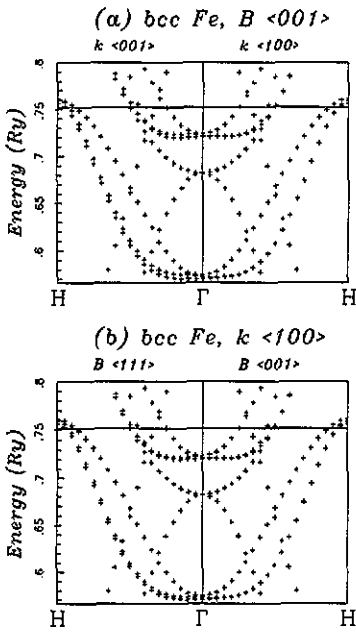


Figure 1. Energy band structure of bcc Fe, calculated with a spin-polarized relativistic KKR program using the potential of Moruzzi *et al* (1978). (a) The high symmetry direction ΓH (the coordinate axis) parallel (left) and perpendicular (right) to the direction of the magnetization. (b) The k_x axis for the magnetization pointing in the $[111]$ (left) and $[001]$ directions (right).

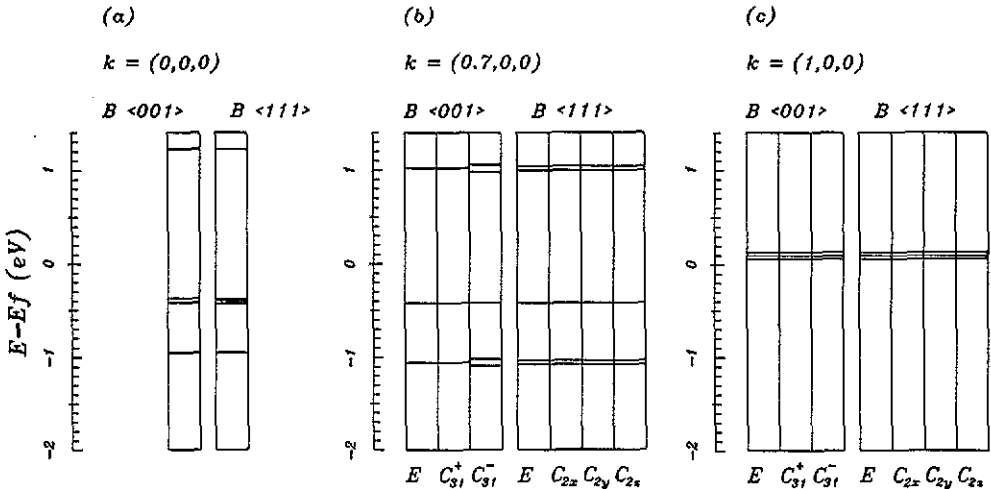


Figure 2. The influence of the direction of magnetization on the energy eigenvalues at some k points situated on the coordinate axes in k space. (a) The Gamma point. (b) In the region of largest band deformations. For each magnetization direction, the eigenvalues are shown for all different inequivalent 1BZ. The group operations below are the corresponding coset representatives of the group Γ in G . (c) The point H at the Brillouin zone boundary.

This method has been applied previously to the anisotropy problem in Ni (Strange *et al* 1989b). It is well known that the crucial point in computing the MAE is the numerical precision of the BZ integral. For orientations of the magnetization along $[001]$ and $[111]$, the calculation was performed even with 210 special directions in

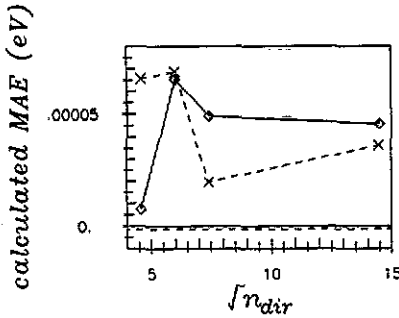


Figure 3. The calculated values of the magnetocrystalline anisotropy energy between [001] and [111] magnetizations, plotted as a function of the square root of the number of special directions in the 1BZ, which is a measure for the angular density of k points. The data points correspond to 21, 36, 55 and 210 directions per 1BZ. ◇: values obtained with the method of special directions. x: values obtained by correcting the integral along one of the special directions (see text). The horizontal broken line indicates the experimental value of $-1.4 \mu\text{eV}$.

one 1BZ. However, as can be seen from figure 3, this was still not enough: the calculated values of the MAE are an order of magnitude larger than the experimental value. The reason for this seems to be that even with many directions, none of the k rays samples directly the boundaries of the 1BZ where the main contributions to the MAE arise. Replacing only one of the directions, that one which is closest to the coordinate axis in k space, by an average over directions within the boundary planes nearby, we obtain a coarsely corrected value which shows a remarkably large shift in the right direction, considering the small percentage of reciprocal space covered by this procedure (figure 3). Clearly, the method of special directions is unable to give a precision as high as required for the magnetic anisotropy problem.

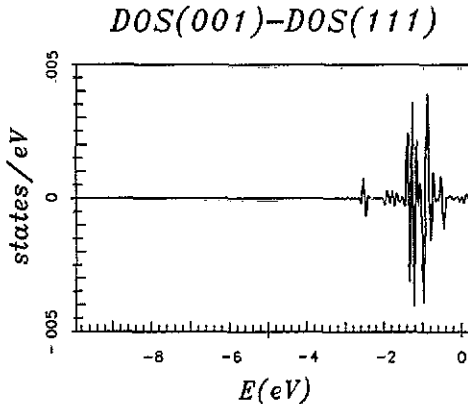


Figure 4. The difference between the densities of states for magnetizations along the [001] and [111] directions. The corresponding scattering path operator was calculated using 210 directions in the 1BZ.

Figure 4 shows the difference of the DOS for the two magnetization directions. The difference is strongly oscillatory and leads to a cancellation effect when integrated over. This explains the small values of the MAE as compared to the shifts in the

energy bands. The energies where the MAE originates are bound to within 2 eV below the Fermi energy, while at E_F itself only very small contributions are found. The anisotropy of the bands themselves extends down to about 3.5 eV below E_F and well above E_F , but the deviations between the different IBZ cancel out in the DOS outside the above mentioned 2 eV interval.

In summary, the MAE seems to originate from regions quite constrained both in k space and energy. Sampling of these regions with high precision might already be sufficient to account for most of the MAE but the method of special directions is not appropriate for this. There are other, more promising techniques, in particular the linear analytic tetrahedron method in its adaptations for the Green function method (Coleridge *et al* 1982, Lambin and Vigneron 1984). This has yet to be installed in the framework of our programs.

4. Conclusions

We have developed a method to treat magnetic symmetry in spin-polarized calculations in a systematic way. The method of Green functions turns out to require some care as compared to the usual band structure methods because of the anti-unitary transformations involved. The integral over the Brillouin zone is reduced to the smallest possible amount of numerical work. In addition, certain matrix properties of the scattering path operator, a representation of the Green function, follow directly by considering the explicit forms of some of the transformation matrices.

An application to the magnetocrystalline anisotropy of Fe shows that the degeneracies in our calculation are correct and maps out the regions in k space and energy where the magnetic anisotropy energy originates; however, the lack of a suitable integration scheme prevents us at present from obtaining a reasonable numerical value for this quantity. The use of better algorithms might help to overcome this deficiency in future calculations.

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Appendix 1. The t matrix under time reversal

The behaviour of the single-site t matrix under time reversal θ requires special consideration since t is influenced by this operation even in the case of a θ -invariant single-site Hamiltonian \hat{H}_s . Indicating operators by hats, we have

$$\hat{\theta}^+ \hat{H}_s \hat{\theta} = \hat{H}_s \quad (\text{A1})$$

$$\hat{t}(z) = \hat{V}_s + \hat{V}_s(z - \hat{H}_s)^{-1} \hat{V}_s \quad (\text{A2})$$

$$\hat{\theta}^+ \hat{t}(z) \hat{\theta} = \hat{V}_s + \hat{V}_s(z^* - \hat{H}_s)^{-1} \hat{V}_s = \hat{t}^+(z). \quad (\text{A3})$$

Thus under time reversal, the t operator is replaced by its Hermitean adjoint. This has to do with the fact that the retarded and advanced boundary conditions of the Green functions are interchanged by time reversal.

Let \hat{H}_s^\uparrow denote a single-site Hamiltonian with a B_{eff} in a specified direction (the arrow indicates the direction of the magnetic field and has nothing to do with the spin variables). $\hat{\theta}$ changes \hat{H}_s^\uparrow into \hat{H}_s^\downarrow because the direction of B_{eff} is reversed. A transformation with $\hat{\theta}$ now yields

$$\hat{\theta}^\dagger \hat{H}_s^\uparrow \hat{\theta} = \hat{H}_s^\downarrow \quad (\text{A4})$$

$$\hat{t}^\uparrow(z) = \hat{V}_s^\uparrow + \hat{V}_s^\uparrow(z - \hat{H}_s^\uparrow)^{-1} \hat{V}_s^\uparrow \quad (\text{A5})$$

$$\hat{\theta}^\dagger \hat{t}^\uparrow(z) \hat{\theta} = \hat{V}_s^\downarrow + \hat{V}_s^\downarrow(z^* - \hat{H}_s^\downarrow)^{-1} \hat{V}_s^\downarrow = [\hat{t}^\downarrow(z)]^\dagger. \quad (\text{A6})$$

On the other hand, a twofold rotation $C_{2\perp}$ perpendicular to B_{eff} also changes \hat{H}_s^\uparrow into \hat{H}_s^\downarrow , thus

$$\hat{C}_{2\perp}^\dagger \hat{t}^\uparrow \hat{C}_{2\perp} = \hat{t}^\downarrow. \quad (\text{A7})$$

In matrix representation, equations (A6) and (A7) are of the form (see appendix 2)

$$t^{\downarrow\dagger} = D(\theta^{-1}) t^{\uparrow\dagger} D^*(\theta)$$

$$t^\downarrow = D(C_{2\perp}^{-1}) t^\uparrow D(C_{2\perp}). \quad (\text{A8})$$

The inverse of the twofold rotation is shown explicitly to keep track of the phase factors which arise in the half-integral representations of the rotation group. The combination of the equations in (A8) yields

$$D(C_{2\perp}^{-1}) t^\uparrow D(C_{2\perp}) = D(\theta^{-1}) t^{\uparrow\dagger} D^*(\theta) \quad (\text{A9})$$

where we have made use of the identity $D^\dagger(\theta) = D^*(\theta^{-1})$. Alternatively, equation (A9) can be written as

$$t^\uparrow = D(C_{2\perp} \theta^{-1}) t^{\uparrow\dagger} D^*(\theta C_{2\perp}^{-1}). \quad (\text{A10})$$

In the single-site case, which apart from the magnetic field is assumed to be spherically symmetric, we can always choose the axis of $C_{2\perp}$ to lie in the xy plane. Then the transformation matrix $D(C_{2\perp} \theta^{-1})$, in a relativistic basis as defined below, is diagonal with elements $(-1)^{l-\mu+1/2} e^{-i2\alpha\mu}$, where α is the angle between the rotation axis and the x axis. Thus the matrix elements in equation (A10) are related by

$$t_{\kappa\mu, \kappa'\mu'} = (-1)^{l-\mu+1/2} e^{-i2\alpha\mu} t_{\kappa'\mu', \kappa\mu} (-1)^{-l'+\mu'-1/2} e^{i2\alpha\mu'} \quad (\text{A11})$$

which strongly resembles the usual reciprocity relation in the absence of a magnetic field. Taking the field to point in the z direction, the only elements that do not vanish are those with $l' = l, l' = l \pm 2$ and $\mu' = \mu$ (Feder *et al* 1983, Strange *et al* 1984), so the phase factors in equation (A11) cancel and the t matrix is symmetric. For other orientations of B_{eff} , this is in general no longer the case. One can also see this from the fact that the single-site t matrix for any chosen orientation of the magnetic field can be obtained from that of another one by a unitary transformation. Transforming a symmetric matrix with a unitary matrix in general destroys the symmetry.

The fact that the S and t matrices can be symmetric is a consequence of time reversal symmetry of the Hamiltonian which shows up in the reciprocity of the t matrix (see e.g. Newton 1966). However, we see that the symmetry of the t matrix still holds when the time reversal symmetry is broken by a magnetic field of uniform orientation, provided that the axis of quantization coincides with the field orientation.

Appendix 2. Matrix representation of antilinear transformations

The operation of time reversal as well as products of it with any spatial transformation are anti-unitary, i.e. unitary and antilinear. An antilinear operator \hat{K} has the property

$$\hat{K}(a\phi + b\psi) = a^* \hat{K}\phi + b^* \hat{K}\psi \quad (\text{A12})$$

where ϕ, ψ are vectors in the space on which \hat{K} is defined, and a, b are complex numbers. The use of antilinear operators requires some care since the usual bra-ket symbols are meaningless in this case (see e.g. Messiah 1961). We define the matrix representation of the time reversal operation to be

$$D_{ij}(\theta) = (\phi_i, \hat{\theta}\phi_j) \quad (\text{A13})$$

with some basis $\{\phi_i\}$. Matrix transformations with antilinear operations are of the form

$$\begin{aligned} \hat{A}' &= \hat{\theta} \hat{A} \hat{\theta}^{-1} && \text{(operators)} \\ A' &= D(\theta) A^* D^*(\theta^{-1}) && \text{(matrices).} \end{aligned} \quad (\text{A14})$$

The complex conjugations obey a formal rule which is generally valid. Let us call the matrix representation of an antilinear operator an antilinear matrix. If such an antilinear matrix occurs in a product of several transformation matrices, then all the matrices on its right-hand side, linear or antilinear, have to be taken complex conjugate. This implies that to the right of an odd number of antilinear matrices, complex conjugation occurs, whereas to the right of an even number of antilinear matrices everything is unchanged. This rule arises from the antilinear property of the operators which change complex numbers into their conjugates; it also applies to the magnetic co-representations of the magnetic groups (see e.g. Bradley and Cracknell 1972). From $\theta\theta^{-1} = 1$ and the fact that the matrix $D(\theta)$ is unitary, it follows that

$$D(\theta)D^*(\theta^{-1}) = 1 \quad (\text{A15})$$

$$D^*(\theta^{-1}) = D^+(\theta). \quad (\text{A16})$$

Throughout this work, spin spherical harmonics are used as basis functions which are defined as

$$\chi_{\kappa\mu}(\Omega) = \sum_{s=\pm 1/2} C(l, 1/2, j; \mu - s, s) Y_{l, \mu - s}(\Omega) \chi_s \quad (\text{A17})$$

where χ_s are the usual basis spinors. The various quantum numbers are related by

$$l = \begin{cases} \kappa & \kappa > 0 \\ \kappa - 1 & \kappa < 0 \end{cases} \quad (\text{A18})$$

$$j = |\kappa| - 1/2 \quad (\text{A19})$$

$$S_\kappa = \text{sign}(\kappa). \quad (\text{A20})$$

For the spherical harmonics, the Condon and Shortley phase convention is used. With the definition of the time reversal operator,

$$\hat{\theta} = -i\sigma_y \hat{K} \quad (\text{A21})$$

where \hat{K} is the complex conjugation operator, the matrix representation of $\hat{\theta}$ in the basis of the $\chi_{\kappa\mu}$ is given by

$$D_{\kappa\mu, \kappa'\mu'}(\theta) = i\delta_{\kappa\kappa'}\delta_{\mu, -\mu'} S_{\kappa}(-1)^{\mu+1/2}. \quad (\text{A22})$$

The next step is to set up the transformation matrix for the operation $C_t = C_{2\perp} \theta^{-1} I$. The unitary rotation matrices in the Condon–Shortley phase convention are given by Altmann (1986). By restricting the axis of $C_{2\perp}$ to be perpendicular to the z direction, with α denoting its angle to the x axis, the matrix $D(C_{2\perp})$ for half-integral representations $j = |\kappa| - 1/2$ is given by

$$D_{\mu\mu'}^j(C_{2\perp}) = \delta_{\mu, -\mu'} i(-1)^{|\kappa|} e^{-i2\alpha\mu}. \quad (\text{A23})$$

The matrix representation of the inversion is the parity, given by $(-1)^l$, viewed as a diagonal matrix. The matrix $D(C_t)$ is thus diagonal and given by

$$D_{\kappa\mu, \kappa'\mu'}(C_t) = \delta_{\kappa\kappa'}\delta_{\mu\mu'}(-1)^{-\mu+1/2} e^{-i2\alpha\mu}. \quad (\text{A24})$$

Its inverse is given by $D^*(C_t^{-1}) = D^+(C_t)$.

For the sake of completeness, we also give the matrices in the non-relativistic case. The time reversal operator is then simply the complex conjugation operator \hat{K} . In the basis of spherical harmonics, and employing again the Condon and Shortley convention,

$$D_{l'm, l'm'}^{\text{NR}}(\theta) = (-1)^m \delta_{ll'} \delta_{m, -m'} \quad (\text{A25})$$

$$D_{m'm}^l{}^{\text{NR}}(C_{2\perp}) = \delta_{m, -m'} (-1)^l e^{-i2\alpha m} \quad (\text{A26})$$

$$D_{l'm, l'm'}^{\text{NR}}(C_t) = \delta_{ll'} \delta_{m'm'} (-1)^m e^{-i2\alpha m}. \quad (\text{A27})$$

Appendix 3. Transformation of the structure constants

The free Green function in a lattice corresponding to a certain k vector can be written as (Kohn and Rostoker 1954)

$$G(k, r - r') = -\frac{1}{\tau} \sum_n \frac{\exp[i(K_n + k)(r - r')]}{(K_n + k)^2 - E} \quad (\text{A28})$$

If g is some point operation which leaves the lattice invariant, then

$$G(gk, g(r - r')) = G(k, r - r'). \quad (\text{A29})$$

The structure constants $B_{LL'}(\mathbf{k}, E)$ are defined by the expansion

$$G(\mathbf{k}, \mathbf{r} - \mathbf{r}') = \sum_{LL'} \left[i^{l-l'} B_{LL'}(\mathbf{k}, E) j_l(\kappa r) j_{l'}(\kappa r') + \kappa \delta_{LL'} j_l(\kappa r) n_l(\kappa r') \right] \\ \times Y_L(\hat{r}) Y_{L'}^*(\hat{r}') \quad \text{for } r < r' < r_i \quad (\text{A30})$$

(Kohn and Rostoker 1954), where $\kappa = \sqrt{E}$ and r_i is the radius of the sphere inscribed into the Wigner-Seitz cell. Using the invariance equation (A29) in the expansion (A30) and the transformation properties of the spherical harmonics,

$$Y_{lm}(g\hat{r}) = g^{-1} Y_{lm}(\hat{r}) = \sum_{m'} Y_{lm'}(\hat{r}) D_{m'm}^l(g^{-1}) \quad (\text{A31})$$

it is clear that the structure constants must transform as

$$B(g\mathbf{k}, E) = D(g) B(\mathbf{k}, E) D(g^{-1}). \quad (\text{A32})$$

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