Multiple-scattering theory of x-ray magnetic circular dichroism

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Résumé : This chapter describes a Green function method to include relativistic corrections into the calculation of x-ray absorption spectra. Expansion up to $(1/c^2)$ enables us to calculate magnetic circular dichroism. Calculation is compared with experiments for Gd and Fe near the edge and in the EXAFS regions

1 Introduction

For the $L_{II,III}$ edges of heavy transition metals and the K-edges of all elements, and for the high-energy range, a multiple-scattering approach is required for the calculation of x-ray magnetic circular dichroism (XMCD) spectra, because one must take explicit account of the scattering of the photoelectron by the neighbours. However, we know that XMCD arises from the interplay of spin-polarisation with spin-orbit coupling. Therefore, these two effects must be included in the model. In this chapter, we introduce a semi-relativistic expansion for the Dirac Green function, which offers a compact and accurate way of taking relativistic effects into account. The results of this expansion will be used to calculate XMCD in various situations.

Other formalisms were used to calculate XMCD. Ebert and coll. have used a fully relativistic multiple-scattering method which gives good results near the edge. They have calculated many systems (see Ref.[1] and Ref.[2] for a review), but always in the near edge region. On the other hand, Ankudinov and Rehr have calculated very convincingly the EXAFS region of the MCD $L_{II,III}$ spectra of Gd [3]. However, they can reproduce neither the edge region nor the K-edge yet. We choose to concentrate on the present semi-relativistic method because it gives reasonable results over the whole energy range which is experimentally accessible.

2 The Dirac equation

The Dirac equation is the one-particle relativistic theory of the electron. Full books are now devoted to the Dirac equation [4],[5]. Therefore, this presentation will be very sketchy.

According to Dirac's formalism, an electron is represented by a four-component wave-function (Dirac spinor) $\Psi = (\psi_1, \psi_2, \psi_3, \psi_4)$.

2.1 The free Dirac equation

The free Dirac spinors are solutions of the free Dirac equation:

$$[c(\alpha_x \cdot p_x + \alpha_y \cdot p_y + \alpha_z \cdot p_z) + \beta mc^2]\Psi = E\Psi$$

where c is the light velocity $p = -i\hbar\nabla$, m is the electron mass α_x, α_y, α_z and β are Hermitian 4x4 matrices for which a convenient representation is :

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

I is the 2x2 identity matrix and σ_x, σ_y and σ_z are the Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The meaning of the various components of the Dirac spinor is given by the mean value of some operators. For instance, the spin operators is $\hbar\Sigma/2$ where

$$\mathbf{\Sigma} = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}.$$

Therefore, the spin components ψ_1 and ψ_3 (ψ_2 and ψ_4) correspond to up (down) spins. Moreover, spinors $(1,0,0,0)$ and $(0,1,0,0)$ are eigenstates of the energy with eigenvalue $E = mc^2$, spinors $(0,0,1,0)$ and $(0,0,0,1)$ are eigenstates of the energy with eigenvalue $E = -mc^2$. The first two components (the so-called large components) represent normal electrons, the next two components (small components) represent positrons. The position probability density is $\rho = \sum_{i=1,4} |\psi_i|^2$ and the norm condition is $\int \rho = 1$, the current density is $\mathbf{j} = ec\Psi^\dagger\alpha\Psi$.

For later use, we shall write the free Dirac Hamiltonian as a 2x2 matrix of 2x2 matrices:

$$H_0 = \begin{pmatrix} mc^2 & cD^\dagger \\ cD & -mc^2 \end{pmatrix},$$

where $D = -i\hbar\sigma \cdot \nabla$ and $mc^2 = mc^2 I$.

2.2 Dirac equation with external field

In the local density approximation, the influence of the nuclei and of the other electrons in the sample is represented by a potential $V(\mathbf{r})$. The Dirac equation with potential is

$$H = H_0 + V = \begin{pmatrix} mc^2 + V(\mathbf{r}) & cD^\dagger \\ cD & V(\mathbf{r}) - mc^2 \end{pmatrix},$$

In the following, potential $V(\mathbf{r})$ can be any 2x2 Hermitian matrix but in most practical applications of LDA the spin and space variables are uncoupled and

$$V(\mathbf{r}) = \begin{pmatrix} V^{\uparrow}(\mathbf{r}) & 0 \\ 0 & V^{\downarrow}(\mathbf{r}) \end{pmatrix}$$

the 2x2 potential is split into a potential acting on up spins and a potential acting on down spins. Non-diagonal potentials can be useful to represent magnetic materials with spiral spin structure. The potentials that are allowed by the theory are described in reference [6]. They contain the potentials used in practice: a sum of finite range potentials with a Coulomb singularity.

According to standard results for the Dirac equation [4, 5], the eigenstates of the Dirac equation are the bound states with energies $E_n < mc^2$ and the continuum states with energies above mc^2. When the potential is not very strong, $E_n - mc^2$ is close to the corresponding eigenvalue of the non-relativistic problem $H = -\hbar^2\Delta/2m + V(\mathbf{r})$. Because of this result, the non-relativistic limit of the energy is reached by subtracting mc^2 to the relativistic energy.

2.3 The Dirac Green function

As for the case of the Schrödinger equation, it is possible to define a Green function for the Dirac equation, that we call the Dirac Green function. Since we know that the relativistic energies tend towards the non-relativistic energy plus mc^2, we shall define a modified Dirac Green function by

$$G_D(z) = (z + mc^2 - H)^{-1} = \begin{pmatrix} z - V(\mathbf{r}) & -cD^{\dagger} \\ -cD & z + 2mc^2 - V(\mathbf{r}) \end{pmatrix}^{-1}. \quad (1)$$

Using this Green function, the absorption cross section is

$$\sigma(\omega) = -4\pi\alpha_0\hbar\omega \sum_i \langle I|(\hat{\epsilon}^*.\mathbf{r})\,\mathrm{Im}G_D(z)(\hat{\epsilon}.\mathbf{r}')|I\rangle,$$

where $|I\rangle$ is a Dirac spinor of one of the initial states, E_i and $z = E_i + \hbar\omega$ are the initial and final states energies referred to mc^2. The sum over i is the sum over initial states of the same energy. $\hat{\epsilon}$ describes the polarisation state of the x-rays and $\mathrm{Im}G_D(z) = \lim_{\eta\to 0}(G_D(z+i\eta) - G_D(z-i\eta))/(2i)$. This last equality is deduced from the completeness relation $\sum_E \psi_i(\mathbf{r}; E)\psi_j^*(\mathbf{r}'; E) = \delta_{ij}\delta(\mathbf{r} - \mathbf{r}')$.

3 The semi-relativistic expansion

In this section, we give a detailed derivation of the semi-relativistic expansion of the Dirac Green function. This can be useful since it is the basis of our treatment of relativistic corrections and since the derivation given in Ref.[6] is not very detailed. We start from the full Green function (1), and we split $z + mc^2 - H$ as follows:

$$\begin{aligned}(z + mc^2 - H) &= \begin{pmatrix} z & -cD^{\dagger} \\ -cD & 2mc^2 \end{pmatrix} + \begin{pmatrix} -V & 0 \\ 0 & z - V \end{pmatrix} \\ &= \begin{pmatrix} z & -cD^{\dagger} \\ -cD & 2mc^2 \end{pmatrix} \left[1 + \begin{pmatrix} z & -cD^{\dagger} \\ -cD & 2mc^2 \end{pmatrix}^{-1} \begin{pmatrix} -V & 0 \\ 0 & z - V \end{pmatrix}\right]\end{aligned}$$

Therefore, the full Green function $G_D = (z + mc^2 - H)^{-1}$ can be written as the product:

$$G_D = \left[1 + \begin{pmatrix} z & -cD^\dagger \\ -cD & 2mc^2 \end{pmatrix}^{-1} \begin{pmatrix} -V & 0 \\ 0 & z - V \end{pmatrix}\right]^{-1} \begin{pmatrix} z & -cD^\dagger \\ -cD & 2mc^2 \end{pmatrix}^{-1} \tag{2}$$

A direct inversion leads to

$$\begin{pmatrix} z & -cD^\dagger \\ -cD & 2mc^2 \end{pmatrix}^{-1} = \begin{pmatrix} G_0 & \frac{1}{2mc}D^\dagger G_0 \\ \frac{1}{2mc}DG_0 & \frac{z}{2mc^2}G_0 \end{pmatrix} \tag{3}$$

where $G_0 = (z + \hbar^2\Delta/(2m))^{-1} = 2m(2mz - D^2)^{-1}$ is the free Green function for the Schrödinger equation. We used the identity $D^\dagger D = DD^\dagger = -\hbar^2\Delta$.

We start now a series of brilliant transformations that lead to a particularly simple expression for the semi-relativistic expansion. On introducing eq.(3) into eq.(2) we obtain,

$$G_D = \left[1 + \begin{pmatrix} -G_0V & \frac{1}{2mc}D^\dagger G_0(z-V) \\ -\frac{1}{2mc}DG_0V & \frac{z}{2mc^2}G_0(z-V) \end{pmatrix}\right]^{-1} \begin{pmatrix} G_0 & \frac{1}{2mc}D^\dagger G_0 \\ \frac{1}{2mc}DG_0 & \frac{z}{2mc^2}G_0 \end{pmatrix}.$$

Between the product of two matrices in the right-hand side of the last equation, we introduce

$$1 = \begin{pmatrix} (1-G_0V)^{-1} & 0 \\ 0 & 1 \end{pmatrix}^{-1} \begin{pmatrix} (1-G_0V)^{-1} & 0 \\ 0 & 1 \end{pmatrix}. \tag{4}$$

Using the identity $(1+a)^{-1}b^{-1} = (b+ba)^{-1}$, the first term in eq.(4) is introduced into the inverse, then the second term multiplies the right matrix, so that

$$G_D = \left[1 + \begin{pmatrix} 0 & \frac{1}{2mc}GD^\dagger(z-V) \\ -\frac{1}{2mc}DG_0V & \frac{z}{2mc^2}G_0(z-V) \end{pmatrix}\right]^{-1} \begin{pmatrix} G & \frac{1}{2mc}GD^\dagger \\ \frac{1}{2mc}DG_0 & \frac{z}{2mc^2}G_0 \end{pmatrix}, \tag{5}$$

where we used $D^\dagger G_0 = G_0 D^\dagger$ and $(1-G_0V)^{-1}G_0 = G$, where G is the Green function of the Schrödinger equation with potential V. In fact, G is a set of two Green functions,

$$G = \begin{pmatrix} G^\uparrow & 0 \\ 0 & G^\downarrow \end{pmatrix}$$

where each Green function corresponds to the Schrödinger equation for the potential with the corresponding spin.

Finally, between the two matrices, we introduce

$$1 = \begin{pmatrix} 1 & 0 \\ \frac{1}{2mc}DG_0V & 1 \end{pmatrix}^{-1} \begin{pmatrix} 1 & 0 \\ \frac{1}{2mc}DG_0V & 1 \end{pmatrix}$$

Again, the first term is introduced into the inverse, the second term multiplies the right matrix, so that

$$G_D = \left[1 - \begin{pmatrix} 0 & \frac{1}{2mc}GD^\dagger(V-z) \\ 0 & \frac{1}{(2mc)^2}[DGD^\dagger + 2m](V-z) \end{pmatrix}\right]^{-1} \begin{pmatrix} G & \frac{1}{2mc}GD^\dagger \\ \frac{1}{2mc}DG & \frac{1}{(2mc)^2}[DGD^\dagger + 2m] \end{pmatrix} \tag{6}$$

where we have used the following identities: $G_0VG = G - G_0$, $DD^\dagger G_0 = 2mzG_0 - 2m$. The advantages of this last form are manyfold. It is written in terms of the full non-relativistic Green function G, so that the effect of the neighbours is taken into account and the semi-relativistic expansion is easily calculated by $(1-T)^{-1} = \sum_n T^n$. Because of the simple form of T, it is possible to write down immediately the general term of the expansion for $n \geq 1$:

$$T^n = \begin{pmatrix} 0 & XY^{n-1} \\ 0 & Y^n \end{pmatrix}, \text{with } X = \frac{1}{2mc} G D^\dagger (V-z) \text{ and } Y = \frac{1}{(2mc)^2}[DGD^\dagger + 2m](V-z).$$

For the sake of comparison, it can be noticed that Morrison et Moss [7] have calculated the relativistic corrections for hydrogen with the Foldy-Wouthuysen method. At the order $1/c^2$ they obtain four terms (three of them can be combined into the Darwin and spin-orbit corrections), at the order $1/c^4$ they obtain eleven terms, at the order $1/c^6$ they obtain thirty terms, and then they stopped. Moreover, most of their terms are singular, whereas all the terms of the expansion (6) are regular.

4 Relativistic effects in absorption

In this section, we describe the various components that enter the absorption cross section. The relativistic absorption cross section is given by

$$\sigma(\hat{\epsilon}) = -4\pi\alpha_0\hbar\omega[\langle I|\hat{\epsilon}^*.\mathbf{r}G^D(E_i+\hbar\omega+i0)\hat{\epsilon}.\mathbf{r}'|I\rangle - \langle I|\hat{\epsilon}^*.\mathbf{r}G^D(E_i+\hbar\omega-i0)\hat{\epsilon}.\mathbf{r}'|I\rangle]/(2i),$$

where $|I\rangle$ is the core state and E_i its energy. In the next section, the relativistic core state is described, then the semi-relativistic expansion of the Green function is used.

4.1 Initial states

In the case of absorption, the initial states $|I\rangle$ are eigenstates of a spherically symmetric core potential. Therefore, [4] they can be written as

$$|I\rangle = \begin{pmatrix} |\psi^+\rangle \\ |\psi^-\rangle \end{pmatrix}$$

where the two-components spinors $|\psi^+\rangle$ and $|\psi^-\rangle$ are the large and small components, respectively. The initial states are eigenvalues of J^2 and J_z. For a K-edge, we have $\ell = 0$, $s = 1/2$ and $j = 1/2$. For a $L_{\rm II}$ edge ($L_{\rm III}$ edge), we have $\ell = 1$, $s = 1/2$ and $j = 1/2$ ($j = 3/2$). For the initial state $j = \ell + 1/2$ and $m_j = m$ the large and small components are $|\psi^+\rangle = (F(r)/r)|\Phi^+_{\ell m}\rangle$, $|\psi^-\rangle = i(G(r)/r)|\Phi^-_{\ell+1 m}\rangle$, where the two-component spinors are

$$|\Phi^+_{\ell m}\rangle = \sum_{m_\ell m_s} (\ell m_\ell s m_s|jm) Y_\ell^{m_\ell}|m_s\rangle \tag{7}$$

$$|\Phi^-_{\ell+1 m}\rangle = \sum_{m_\ell m_s} (\ell+1 m_\ell s m_s|jm) Y_{\ell+1}^{m_\ell}|m_s\rangle, \tag{8}$$

where $(\ell m_\ell s m_s|jm)$ is a Clebsch-Gordan coefficient. The exponent $\pm$ in the definition of $|\Phi^\pm_{\ell m}\rangle$ indicates that $j = \ell \pm 1/2$. Similarly, the initial state for $j = \ell - 1/2$, $m_j = m$ can be written $|\psi^+\rangle = (F(r)/r)|\Phi^-_{\ell m}\rangle$, $|\psi^-\rangle = i(G(r)/r)|\Phi^+_{\ell-1 m}\rangle$.

The normalisation condition is $\int_0^\infty F^2(r) + G^2(r) = 1$. $F(r)$ is the amplitude of the large (electron) component, $G(r)$ is the amplitude of the small (positron) component. These wavefunctions are plotted in Fig.1 for the $L_{\rm II}$ and $L_{\rm III}$ edges of gadolinium, and in Fig.2 for the K edge of iron, where it can be seen that the small components is not negligible.

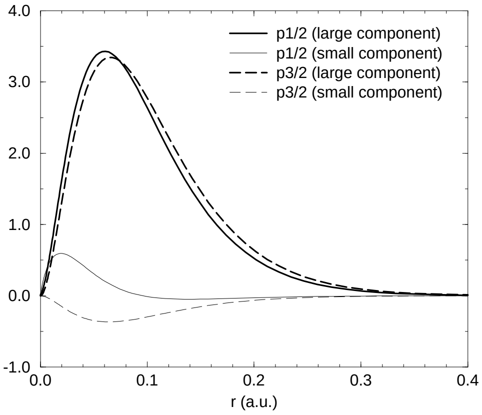

FIG. 1 - $2p_{1/2}$ *and* $2p_{3/2}$ *relativistic wave functions for Gd.*

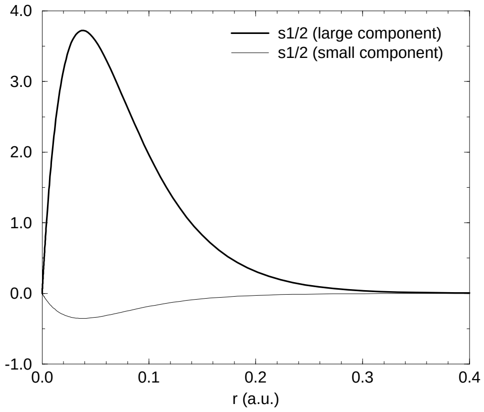

FIG. 2 - $1s_{1/2}$ *relativistic wave functions for Fe.*

4.2 Expansion of the Green function

Using the initial states of the previous section, and making the semi-relativistic expansion of the Dirac Green function up to $(1/c^2)$, we obtain the semi-relativistic cross-section:

$$\begin{aligned} \langle I|\hat{\epsilon}^*.\mathbf{r}G_D\hat{\epsilon}.\mathbf{r}'|I\rangle &\simeq \langle\psi^+|\hat{\epsilon}^*.\mathbf{r}G\hat{\epsilon}.\mathbf{r}'|\psi^+\rangle \\ &+ \frac{1}{2mc}\langle\psi^+|\hat{\epsilon}^*.\mathbf{r}GD^\dagger\hat{\epsilon}.\mathbf{r}'|\psi^-\rangle + \frac{1}{2mc}\langle\psi^-|\hat{\epsilon}^*.\mathbf{r}DG\hat{\epsilon}.\mathbf{r}'|\psi^+\rangle \\ &+ \frac{1}{(2mc)^2}\langle\psi^+|\hat{\epsilon}^*.\mathbf{r}GD^\dagger(V-z)DG\hat{\epsilon}.\mathbf{r}'|\psi^+\rangle \\ &+ \frac{1}{(2mc)^2}\langle\psi^-|\hat{\epsilon}^*.\mathbf{r}(DGD^\dagger+2m)\hat{\epsilon}.\mathbf{r}|\psi^-\rangle. \end{aligned} \tag{9}$$

When investigating the relativistic corrections to x-ray absorption spectra, all terms in eq.(9) should be kept. When one is only interested in the magnetic circular dichroism of powders, a number of terms fall out. At this step, it is convenient to distinguish between the $\mathrm{L_{II,III}}$ edges and the K-edges.

4.3 $\mathrm{L_{II,III}}$ edges

At the $\mathrm{L_{II,III}}$ edges, the first term in eq.(9) gives a contribution to MCD. Therefore, we shall start from the simplest case for which we keep only this term. Using the explicit form for Clebsch-Gordan coefficients, we arrive at the following cross-sections for left (σ^+) and right (σ^-) circularly-polarised x-rays at the $\mathrm{L_{II}}$ edge

$$\begin{aligned} \sigma^+ &= \sigma^\uparrow + 3\sigma^\downarrow \\ \sigma^- &= 3\sigma^\uparrow + \sigma^\downarrow \end{aligned}$$

and at the $\mathrm{L_{III}}$ edge

$$\begin{aligned} \sigma^+ &= 5\sigma^\uparrow + 3\sigma^\downarrow \\ \sigma^- &= 3\sigma^\uparrow + 5\sigma^\downarrow. \end{aligned}$$

In the lecture on the Green function, it was observed that the Green function for the absorbing site i is the sum of a local Green function, corresponding to the isolated i-th atom, plus a function which represents the influence of the neighbours. Because of this decomposition, the absorption cross-section will be written, for each spin, as $\sigma = \mathrm{Im}(\tilde\sigma_a) + \mathrm{Im}(\tilde\sigma_l)$. $\tilde\sigma_a$ is the absorption due to the isolated photoabsorbing atom:

$$\tilde\sigma_a(z) = (4\pi\alpha_0/9)(z - E_i)i\sqrt{z}\exp[i\delta_2^0(z)]D^H(z)$$

and $\tilde\sigma_l$ is the contribution of the neighbours which gives an additional local density of d states projected on the absorbing atom:

$$\tilde\sigma_l(z) = (4\pi\alpha_0/9)(z - E_i)\sqrt{z}D^2(z)\exp[i\delta_2^0(z)]\frac{\check\tau^{00}(22,00;z)}{\sqrt{5}\sin\delta_2^0(z)} .$$

We have defined $\check\tau^{0j}(\ell\ell', a\alpha; z) = \sum_{mm'}(-1)^{(\ell-m)}(\ell{-}m\ell'm'|a\alpha)\tilde\tau^{0j}_{\ell m\ell'm'}(z)$, and the radial integrals are $D(z) = \int_0^\infty r^2 dr F(r)R_2^0(r;z)$, where $F(r)$ is the large component of the $2p$ wave function and $D^H(z) = \int_0^\infty r^2 dr F(r)\phi(r;z)$ where we have defined an auxiliary function $\phi(r;z) = \int_0^\infty r'^2 dr' F(r')R_2^0(r_<;z)H_2^0(r_>;z)$. R_2^0 and H_2^0 are solutions of the radial Schrödinger equation for the spherical potential of the absorbing atom with $\ell = 2$, such that $R_2^0(r)$ is regular at the origin and matches smoothly to $\cos\delta_\ell^i j_\ell(\kappa r) - \sin\delta_\ell^i n_\ell(\kappa r)$ at the muffin-tin radius, and $H_2^0(r)$ matches smoothly to $h_2^+(\kappa r)$ at the muffin-tin radius.

4.4 K edges

The case of a K-edge is more complicated, because the first term in eq.(9) gives no dichroism. It can be shown that the only term that gives rise to magnetic circular dichroism is $\frac{1}{(2mc)^2}\langle\phi|\hat\epsilon^*\cdot\mathbf{r}GD(V-z)DG\hat\epsilon\cdot\mathbf{r}'|\phi\rangle$. The expression is further simplified by noticing that $D(V-z)D = -\hbar^2[(\nabla V\cdot\nabla) + (V-z)\Delta + i\sigma\cdot(\nabla V\times\nabla)]$ and the only term that plays a role in MCD is the standard spin-orbit term for spherical potentials:

$$-\hbar^2 i\sigma\cdot(\nabla V\times\nabla) = \frac{\alpha_0^2 a_0^2}{4}\frac{1}{r}\frac{dV}{dr}\ell\cdot\sigma = \xi(r)\ell\cdot\sigma.$$

The effect of the spin-orbit interaction on MCD is now written as $GD(V-z)DG \to G\xi(r)\ell\cdot\sigma G$. We have seen in the lecture on the Green function that the Green function is the sum of a local term and a neighbour term when both arguments of the Green function belong to the same site, and is just a neighbour term when the two arguments belong to different centers. The spin-orbit should act on all centers. Because of the form of the Green function, we can write the MCD spectrum as a sum of three terms: the magnetic circular dichroic spectrum of a powder is:

$$\sigma_{MCD} = \sigma^- - \sigma^+ = \mathrm{Im}\Big[\sum_s((-1)^{(s-1/2)}(\tilde\sigma^s_{1a}(E+i\Gamma) + \tilde\sigma^s_{1l}(E+i\Gamma) + \tilde\sigma^s_{1n}(E+i\Gamma))\Big]$$

where $\tilde\sigma_{1a}(z) = -(8\pi\alpha_0/3)(z - E_i)z\exp[2i\delta_1^0(z)]M^{HH}(z)$ describes the purely atomic contribution to MCD (the Fano effect),

$$\tilde\sigma_{1l}(z) = (8\pi\alpha_0/3)(z - E_i)2iz\exp[2i\delta_1^0(z)]D(z)M^H(z)\frac{\check\tau^{00}(11,00;z)}{\sqrt{3}\sin\delta_1^0(z)}$$

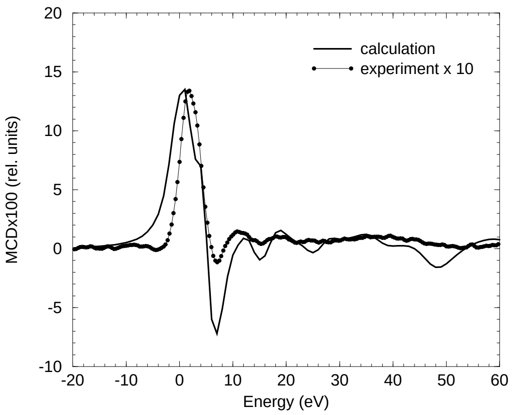

FIG. 3 - *Comparison between calculation and experiment at the L_{III} edge of Gd*

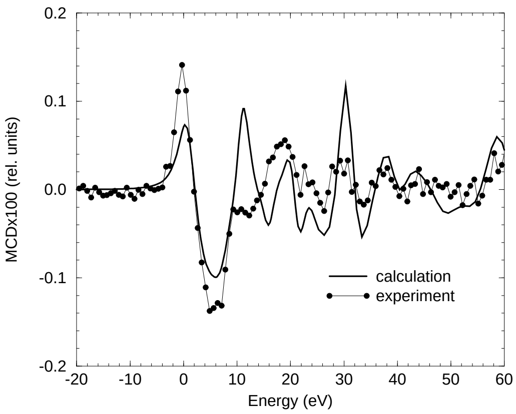

FIG. 4 - *Comparison between calculation and experiment at the K edge of Fe*

is the local contribution due to the spin-polarization of the p-states on the absorbing site, and

$$\begin{aligned}\tilde{\sigma}_{1n}(z) &= -(8\pi\alpha_0/3)(z-E_i)zD^2(z)\sum_{j\ell}\frac{(-1)^\ell}{12}\exp[i(\delta_1^0(z)+\delta_\ell^j(z))]\zeta_\ell^j(z)\\ &\times \sum_{a=|\ell-1|}^{\ell+1}[(\ell-a)(\ell+a+1)+2]\sum_\alpha(-1)^{a-\alpha}\frac{\check{\tau}^{0j}(1\ell,a\alpha;z)\check{\tau}^{0j}(1\ell,a-\alpha;z)}{\sin\delta_1^0(z)\sin\delta_\ell^j(z)}\end{aligned}$$

describes the contribution to MCD due to the spin-orbit scattering of the photoelectron by the neighbours and the absorber. The radial matrix elements are $M^H(z) = \int_0^\infty r^2 dr\xi(r)R_1^0(r;z)\phi(r;z)$, where the auxiliary function $\phi(r;z)$ is defined as for a $L_{\text{II,III}}$ edge and $M^{HH}(z) = \int_0^\infty r^2 dr\xi(r)\phi^2(r;z)$ and the spin-orbit parameter is defined for each ℓ and each atomic site j as $\zeta_\ell^j(z) = \int_0^\infty r^2 dr\xi^j(r)\left[R_\ell^j(r;z)\right]^2$. The present equations correct a mistake by a factor of -2 in Ref. [8].

5 Results near the edge

In this section, we shall compare the calculation with experimental results for Gd and Fe near the edge. This region is notoriously difficult to calculate, even for standard spectra. Therefore, we do not expect a good agreement.

5.1 L_{III} edge of gadolinium

The results obtained for the L_{III} edge of hcp-gadolinium are presented in Fig.3. Experiment was carried out on a thin layer of gadolinium at 10K. The overall agreement is fair. Many additional effects are supposed to play some role in the edge region, such as quadrupole transitions or multiplet effects. The results for gadolinium are surprisingly good, and such an agreement is not to be expected for the other rare earths.

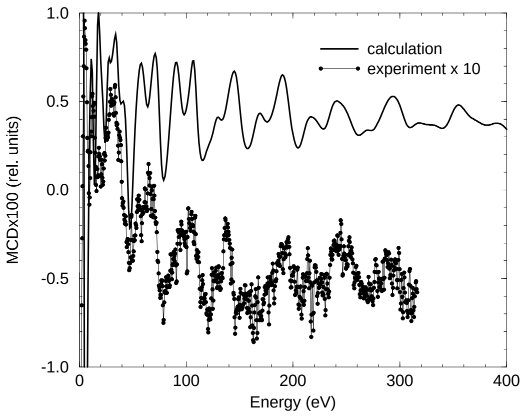

FIG. 5 - *Comparison between calculation and experiment for EXAFS at the L_{III} edge of Gd*

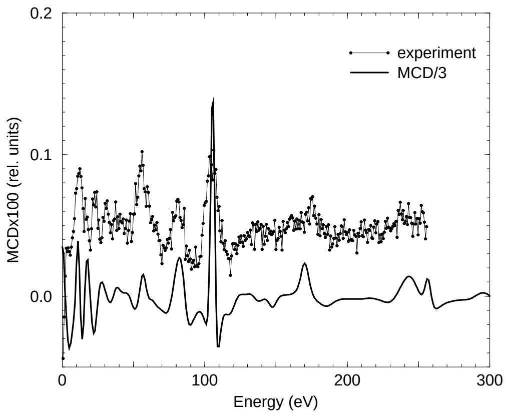

FIG. 6 - *Comparison between calculation and experiment for EXAFS at the K edge of Fe*

5.2 K edge of iron

The results obtained for the K edge of bcc-iron are presented in Fig.4. The calculation was carried out on a cluster of 259 atoms.

For iron, the overall shape of the edge region is correctly reproduced, although the intensity is too small. The second positive peak of the calculation is not present in the experimental spectrum. It is generally observed that the region between 10 eV and 30 eV above the edge is not well reproduced. Various causes are possible, such as an incorrect potential, or a bad treatment of the inelastic collisions of the photoelectron. A better potential can be obtained by carrying out a non-muffin-tin calculation. This work is in progress.

6 Magnetic EXAFS

In the EXAFS region, spurious effects, such as quadrupole transitions or multiplet effects are not expected to play any role, and the multiple-scattering treatment gives excellent results for the calculation of normal spectra. However, MCD effects are due to tiny differences between the potentials for up and down electrons and XMCD spectra give a very fine criterium to assess the quality of these potentials. Again, we shall compare calculation with experiment for gadolinium and iron.

6.1 L_{III} edge of gadolinium

The comparison of the EXAFS region for hcp-gadolinium is plotted in figure 5. It is observed that the overall shape of the magnetic EXAFS spectrum is correctly reproduced. This suggests that the influence of the spin-orbit interaction on the photoelectron is small. The same is not expected to be true at the $L_{II,III}$ edges of $3d$ transition metals. Because of this agreement, we can be confident in the formalism we use and deduce a direct relation between MCD spectra and spin-polarisation of density of states. The MCD spectrum is broadly equal to the spin-polarisation of the density of states times a fairly constant electric dipole matrix element.

6.2 K edge of iron

The comparison of the EXAFS region for fcc-iron is plotted in figure 6. The agreement is also fair, altough the effect is very small. In the case of the K edges, MCD is not proportional to the spin-polarisation of the density of states. In fact, MCD spectra are here proportional to the derivative of the spin-polarisation. A consequence of this peculiar behaviour, which is different from the case of the $L_{II,III}$ edges, is that MCD spectra at the K-edge are proportional to normal spectra in the EXAFS range [9].

Références

[1] S. Stähler, G. Schütz, and H. Ebert. Magnetic K-edge absorption of 3d elements and its relation to local magnetic structure. *Phys. Rev. B*, 47(2):818–26, 1993.

[2] H. Ebert. Circular magnetic x-ray dichroism in transition metal systems. In H. Ebert and G. Schütz, editors, *Spin-Orbit Influenced Spectroscopies of Magnetic Solids*, volume 466 of *Lecture Notes in Physics*, pages 159–77, Berlin, 1996. Springer.

[3] A. Ankudinov and J.J. Rehr. Calculation of x-ray magnetic circular dichroism of Gd. *Phys. Rev. B*, 52(14):10214–20, 1995.

[4] B. Thaller. *The Dirac Equation.* Springer, Berlin, 1992.

[5] W. Greiner, B. Müller, and J. Rafelski. *Quantum Electrodynamics of Strong Fields.* Springer, Berlin, 1985.

[6] F. Gesztesy, H. Grosse, and B. Thaller. A rigorous approach to relativistic corrections of bound states for spin-1/2 particles. *Ann. Inst. Henri Poincaré*, 40(2):159–74, 1984.

[7] J.D. Morrison and R.E. Moss. Approximate solution of the dirac equation using the foldy-wouthuysen hamiltonian. *Mol. Phys.*, 41(3):491–507, 1980.

[8] Ch. Brouder, M. Alouani, and K. H. Bennemann. Multiple-scattering theory of x-ray magnetic circular dichroism: Implementation and results for iron K-edge. *Phys. Rev. B*, 54(10):7334–49, 1996.

[9] S. Pizzini, A. Fontaine, E. Dartyge, Ch. Giorgetti, F. Baudelet, J.-P. Kappler, P. Boher, and F. Giron. Magnetic circular x-ray dichroism measurements of Fe-Co alloys and Fe/Co multilayers. *Phys. Rev. B*, 50(6):3779–88, 1994.