X-ray magnetic circular dichroism in (Ge,Mn) compounds: Experiments and modeling

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ABSTRACT
X-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) spectra at the L2,3 edges of Mn in (Ge,Mn) compounds have been measured and are compared to the results of first principles calculation. Early ab initio studies show that the Density Functional Theory (DFT) can very well describe the valence band electronic properties but fails to reproduce a characteristic change of sign in the L3 XMCD spectrum of Mn in Ge3Mn5, which is observed in experiments. In this work we demonstrate that this disagreement is partially related to an underestimation of the exchange splitting of Mn 2p core states within the local density approximation. It is shown that the change in sign experimentally observed is reproduced if the exchange splitting is accurately calculated within the Hartree–Fock approximation, while the final states can be still described by the DFT. This approach is further used to calculate the XMCD in different (Ge,Mn) compounds. It demonstrates that the agreement between experimental and theoretical spectra can be improved by combining state of the art calculations for the core and valence states respectively.

1. Introduction

The development of spintronics has emphasized the need for novel materials exhibiting a strong electric-magnetic interplay, as it would permit the design of new devices achieving an electric control of the magnetic properties, strongly spin-polarized currents and magneto-transport effects, or magneto-optical functions.

One class of such materials is that of diluted magnetic semiconductors (DMSs) presenting carrier induced ferromagnetism [1]. Magnetic impurities introduced in II–VI or III–V semiconductors exhibit a strong coupling to the carriers of the semiconductor, giving rise to giant magneto-optical (giant Zeman effect) and magneto-transport properties. If electrically doped, DMSs also feature ferromagnetic interactions [1] that depend on the carrier density in such a way [2] that the Curie temperature [3] and the magnetic anisotropy [4] can be controlled in field effect devices. It was rapidly recognized that in the quest for such materials, methods complementing magnetic studies were needed: the most widely used are magneto-optical spectroscopy (giant Zeeman effect and magnetic circular dichroism at the bandgap), [5] magneto-transport (magnetoresistance, anomalous Hall effect), [6] and x-ray magnetic spectroscopy (x-ray absorption spectroscopy, XAS, and x-ray magnetic circular dichroism, XMCD, at both K and L edges).

XAS and XMCD are two well established techniques for the study of the electronic and magnetic properties of materials. The existence of dichroism sum rules, which have been derived theoretically [7,8] and then successfully applied to XMCD experimental spectra [9], makes it straightforward to extract quantitative information on the local spin and orbital magnetic moments, in particular in the case of the L2,3 absorption edges of the transition metals. There are several efficient ways of calculating the theoretical XAS and XMCD spectra e.g. the multiplet approach for localized systems or the configuration interaction (CI) approach for metal systems, where the hybridization between the transition metal d states and the surrounding delocalized states is taken into account as a superposition of different d configuration (i.e. different multiplet structures) [10]. Additionally the density functional theory (DFT) can accurately describe the valence band electronic properties for both ionic and metallic systems and therefore it can...
also be used to calculate the theoretical XAS and XMCD spectra. Both the sum rules and DFT calculations at the L_{2,3} absorption edges work well for heavier 3d transition metals (i.e., Fe, Co), however they are more difficult to apply to lighter ones [11,12]. A discrepancy as high as 50–80% or even a wrong sign has been reported between the value of the magnetic spin moment in 3d\(\text{Mn}^{3+}\) deduced from the application of the sum rule, and its expectation value (Note that for a 3d\(^5\) system the error is much reduced to a value between 68% and 74% with no wrong sign) [11]. The difficulty in such an approach is that interaction between the photocreated 2p-core hole and the 3d-electrons of Mn modifies considerably the shape of L_{2,3} spectra, leading to multiplet effects [13,14]. These effects are not always caught by DFT, and a disagreement between experimental and theoretical L_{2,3} spectra is often found [14].

As a result, it would be highly desirable to improve the DFT-based XAS and XMCD calculations for lighter transition metals. In particular, Mn is the transition metal impurity which is the most widely used to make DMSs. In II–VI semiconductors such as selenides and tellurides, all compositions up to 100% Mn can be grown by molecular beam epitaxy. The most studied DMS with carrier induced ferromagnetism is (Ga,Mn)As where Mn substitutes Ga. Values of the Curie temperature have been improved but stay lower than 200 K. As this is too low for practical applications, and in order to ensure a good compatibility with silicon technology, some effort has been directed towards introducing Mn into germanium. Recent reports have shown significantly higher Curie temperatures, but also that the distribution of magnetic impurity ions is inhomogeneous [15–17]. Such nanostructures, e.g. inclusions, contain a locally high concentration of Mn ions. Thus the observed high temperature ferromagnetism can be explained by a stronger exchange interaction between Mn ions, which are separated by shorter distances in the inclusion. Nevertheless, interesting magneto-transport properties have been reported. This class of hybrid systems [18] which exhibit high values of the Curie temperature and strong magneto-transport and/or magnetooptical properties, comprises also, e.g., (Zn,Cr)Te [19], (Ga,Mn)N and (Ga,Fe)N [20], and MnAs in GaAs [21], to cite but a few examples.

Our main interest here is driven by understanding the electronic, magnetic and structural properties of self-assembled ferromagnetic (Ge,Mn) nanocolloids, a system in which high, magnetic and structural properties, comprises also, e.g., (Zn,Cr)Te [19], (Ga,Mn)N and (Ga,Fe)N [20], and MnAs in GaAs [21], to cite but a few examples. The experimental lattice parameter of bulk Ge was 5.66 Å was obtained by X-ray diffraction. In this paper we start from the assumption that the exchange interaction between 2p- and 3d-electrons of Mn is weakly screened by valence electrons and we propose to evaluate the splitting of the core states within the Hartree–Fock (HF) approximation, whereas the valence states in metals are still calculated within DFT. We apply this heuristic approach to the calculation of the XAS-XMCD spectra of Mn and test it in the specific case of the ferromagnetic semiconductor (Ge,Mn) and related systems. This is done in a fashion that may be further applied to other systems.

2. Methods

2.1. Experimental

Experimental XAS and XMCD spectra measurements in (Ge, Mn) nanocolumns samples were carried out on 80-nm-thick thin films obtained by low-temperature molecular beam epitaxy. Details on the sample growth can be found in Ref. [26]. The (Ge, Mn) samples were efficiently protected against oxidation by in situ deposition of a 3 nm-thick amorphous Si layer. Measurements were carried out at beamline UE46-PCG at the Helmholtz Center Berlin using the total electron yield method [23]. A magnetic field of 5 T has been applied in the plane of incidence of the x-rays to align the magnetization along the light propagation. The sample temperature was 5 K. Experimental XAS-XMCD spectra in the (Ge,Mn) nanocolumns system are shown in Fig. 1. No saturation effects [31] could be evidenced from measurements at various incidence angles (30°, 60° and 90°).

We also considered XAS-XMCD spectra of the ferromagnetic metal Ge_{3}Mn_{5}, as reported in the literature both for bulk single crystals [32] and for thin films [14,33], see Fig. 1. They appear to be quite similar to those of the (Ge,Mn) nanocolloids.

2.2. Model

We now turn to the calculation of the theoretical XAS/XMCD spectra. To obtain the spectra, a three step calculation was performed: first the crystal potential was accurately calculated ab initio. Ab initio methods are based on an explicit band structure calculation, where hybridization of Mn atoms with neighbor atoms and related charge redistributions are taken into account. This method is therefore more suitable to predict XMCD spectra in compounds with different local atomic structure. Then the exchange interaction in the core states was calculated within the Hartree–Fock approximation which allows for an accurate description of the core states. Finally the theoretical XAS/XMCD spectra were calculated within the multiple scattering approach. Each step is described in details hereafter.

2.2.1. Crystal potential

The crystal potential was obtained from a self-consistent solution of the Kohn–Sham equations within the general gradient approximation (GGA) [38] using the full-potential WIEN2k code [39]. The spherical part of the self-consistent crystal potential in each MT-sphere was retained for the XAS calculations. Then the Schrödinger (or Dirac) equation was solved in each MT-sphere. The experimental lattice parameter of bulk Ge \(a = 5.86\,\text{Å}\) was used in all compounds, except in Ge_{2}Mn_{16} [27], and Ge_{3}Mn_{5},
For the Ge$_2$Mn(C16) compound $a = 5.95$ Å and $c = 5.03$ Å parameters were obtained from a structural relaxation calculation, [27] while experimental values [40] $a = 7.184$ Å and $c = 5.053$ Å were used for Ge$_3$Mn$_5$. In all the structures atomic positions were relaxed, except for Ge$_2$Mn$_2$, where experimental atomic positions were taken from Ref. [40]. Note that a previous calculation shows that a relaxation of internal atomic positions and lattice parameters within GGA does not change the experimental parameters [34,41,42].

In most cases the Kohn–Sham eigenvalues and eigenfunctions, calculated in metals, are rather close to those obtained from the solution of the quasiparticle equation [43]:

\[
\begin{align*}
-\frac{1}{2}V^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{nl}}(\mathbf{r}) \phi_{nk}(\mathbf{r}) \\
+ \sum_{\mathbf{r}', \mathbf{r}} E_{nk} \phi_{nk}(\mathbf{r}') d^* \mathbf{r}' = E_{nk} \phi_{nk}(\mathbf{r}).
\end{align*}
\]

Therefore it is assumed that final state eigenfunctions $\phi_f$ and eigenvalues $E_f$ are well described by DFT in metallic compounds. Meanwhile the DFT eigenvalues of the initial states can be improved, as shown in the next step.

### 2.2.2. Core levels exchange interaction

The initial states in x-ray absorption spectroscopy at the L$_{2,3}$ edges are the 2p core levels of Mn. They are split by the spin—orbit interaction between valence $2p$- and $3d$-electrons of the Mn atom. Considering that the exchange coupling acts only on the spin of the core states, the interaction Hamiltonian can be written as $gS\mathcal{H}_{\text{xc}}$, where $g$ is the electron gyromagnetic factor and $S$ is the spin operator. As a result, the 2p-level with $j = 3/2$ is split into two sublevels $(m_j = -3/2, 1/2, 1/2, 3/2)$ and the 2p-level with $j = 1/2$ is split into four sublevels $(m_j = -1/2, 1/2, -1/2, 1/2)$. The energy splitting between two consecutive sublevels is given in units of $g\mathcal{H}_{\text{xc}}$ by

\[
\frac{1}{2} \left( s(s+1) - l(l+1) \right) \frac{1}{2j(j+1)}
\]

where $s = 1/2$ and $l = 1$ for 2p electronic states. The energy separation of each sublevel is then $-g\mathcal{H}_{\text{xc}}/3$ at the $j = 3/2$ level and $g\mathcal{H}_{\text{xc}}/3$ at the $j = 1/2$ level. Therefore, state $m_j = 3/2$ is the lowest in energy at the 2p$_{3/2}$ level and conversely, state $m_j = -1/2$ is the lowest in energy at the 2p$_{1/2}$ level. Furthermore, the value of $\mathcal{H}_{\text{xc}}$ can be evaluated as a difference between eigenvalues of the 2p-core sublevels and approximating $g$ by 2:

\[
2\mathcal{H}_{\text{xc}} = \epsilon_j^m - \epsilon_j^{m_j}.
\]

If the exchange interaction between the 2p- and 3d-electrons of a Mn atom is weakly screened by valence electrons, a good estimate of the value of the exchange splitting $\mathcal{H}_{\text{xc}}$ can be obtained within the Hartree–Fock approximation, from a calculation of the exchange term in the self-energy:

\[
2\mathcal{H}_{\text{xc}} = \langle \phi_j^m | (\nabla \phi_j^m)^2 | \phi_j^m \rangle - \langle \phi_j^m | V_{\text{tot}} | \phi_j^m \rangle.
\]
equation was solved in each MT-sphere) whereas the spin-orbit splitting of the 2p core states was always taken into account. In order to evaluate the effect of spin–orbit interaction between valence electrons on absorption spectra, fully relativistic calculations of final states in Eq. (5) were also performed.

2.2.3. Absorption and magnetic dichroism spectra

Finally, XAS spectra of (Ge,Mn) compounds have been computed from first principles using the FDMNES code [46]. In the dipole approximation, the x-ray absorption cross-section is given by

$$\sigma(\alpha) = 4\pi^2\epsilon_0 c^2 \sum_{ij}(\phi^*_j \phi_i)^2 \times \delta(\hbar \omega - \epsilon_j - \epsilon_i).$$

(5)

where $\alpha$ is the fine structure constant, $\phi_i$, $\epsilon_i$ and $\phi_j$, $\epsilon_j$ are eigenfunctions and eigenvalues of the initial and final states correspondingly, $\delta_f$ is a Lorentzian curve of width $\Gamma$ determined by the core-hole lifetime, and $\epsilon$ is the photon polarization. The absorption cross-section is calculated for the three orthogonal directions of light propagation ($x, y, z$), and the direction of the magnetization along the light propagation. Then a mean value of the cross-section is evaluated.

The electron final states in the cluster were calculated using the multiple-scattering approach and within the muffin-tin (MT) approximation [47,48]. The calculation was performed in a periodic crystal potential, but scattering paths were considered in a cluster with a diameter of 12 Å.

The XAS and XMCD signals were then evaluated as $(\sigma^+ - \sigma^-)/2$ and $(\sigma^+ + \sigma^-)/2$, respectively, where $\sigma^+$ and $\sigma^-$ are absorption cross-sections for the two circular polarizations of x-ray radiation.

Calculated XAS and XMCD spectrum at the L2,3-edges of Mn is plotted as a function of Mn spin moment in Fig. 2, respectively, where $\delta_f$ is the photon polarization. The XAS and XMCD signals were then evaluated as $(\sigma^+ - \sigma^-)/2$ and $(\sigma^+ + \sigma^-)/2$, respectively, where $\sigma^+$ and $\sigma^-$ are absorption cross-sections for the two circular polarizations of x-ray radiation.

3. Results

3.1. Exchange splitting of 2p-core levels

The exchange splitting $H_{xc}$ in different compounds (these compounds are described in more details in the next sections) was calculated within the GGA and the HF approximation. Calculation parameters and corresponding exchange splitting values are listed in Table 1. $H_{xc}$ is plotted as a function of Mn spin moment in Fig. 2.

3.2. Ge$_3$Mn$_5$: a test material

As mentioned earlier, the intermetallic compound Ge$_3$Mn$_5$ displays experimental XAS-XMCD spectra similar to those observed in the (Ge,Mn) nanocolums (Fig. 1). Accordingly, we start our detailed study by considering this well-known system, which is available in bulk form and as thin epitaxial layers. It has a hexagonal crystal structure with a space group $P6_3/mmc$ and lattice parameters $a=7.184$ Å and $c=5.053$ Å [40]. The primitive cell contains three inequivalent atoms, Mn$_1$, Mn$_2$ and Ge, in positions [34]:

$$4(d)\text{ Mn}_1 \pm (\frac{1}{2}, \frac{1}{3}, 0), \pm (\frac{1}{2}, \frac{1}{3}, \frac{1}{2})$$

$$6(g)\text{ Mn}_2 \pm (x, 0, \frac{1}{3}), \pm (0, \frac{1}{3}, x), \pm (y, y, x), x = 0.2397$$

$$6(g)\text{ Ge} \pm (x, 0, \frac{1}{3}), \pm (0, \frac{1}{3}, x), \pm (y, y, x), x = 0.6030$$

The experimental magnetic spin moments of Mn$_1$ and Mn$_2$ atoms are different: 1.96(3)$\mu_B$ and 3.23(2)$\mu_B$ correspondingly.

![Fig. 2. Exchange splitting of Mn 2p-states in different compounds (see text), calculated within the GGA (circles) and the HF approximation (squares). Numerical values are given in Table 1. The diamond symbol corresponds to the $\alpha$-Ge$_3$Mn compound calculated within the LDA.](image-url)

Table 1: Values of structural and magnetic parameters obtained from the WIEN2K calculation: $R_{MT}$ is the radius of a muffin-tin sphere around the atom; $M_{eff}$ is the magnetic spin moment of the atom, calculated by integration of the spin density over the sphere; $M_{zeff}$ is the magnetic spin moment per formula unit. The last parameter, $2H_{Mn}$, is the splitting parameter introduced in Eq. (4), calculated in the HF approximation. For each compound, the number of atoms of each sort is indicated by the multiplication factor.

<table>
<thead>
<tr>
<th>Calculated parameters</th>
<th>Ge$_3$Mn$_5$</th>
<th>Ge$_3$Mn-α</th>
<th>Ge$_3$Mn-α</th>
<th>Ge$_3$MnCl$_6$</th>
<th>Ge$_3$Mn</th>
<th>Ge$_3$Mn</th>
<th>Ge$_3$Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{MT}$, Å</td>
<td>1.241</td>
<td>1.241</td>
<td>1.241</td>
<td>1.254</td>
<td>1.254</td>
<td>1.281</td>
<td>1.281</td>
</tr>
<tr>
<td>$M_{zeff}$, μB</td>
<td>2.28</td>
<td>3.19</td>
<td>-0.15</td>
<td>1.00</td>
<td>-0.02</td>
<td>2.38</td>
<td>-0.04</td>
</tr>
<tr>
<td>$M_{zeff}$, μB</td>
<td>13.73</td>
<td>0.96</td>
<td>2.19</td>
<td>2.19</td>
<td>1.58</td>
<td>2.98</td>
<td>3.16</td>
</tr>
<tr>
<td>$2H_{Mn}$, eV</td>
<td>1.775</td>
<td>2.420</td>
<td>0.684</td>
<td>1.835</td>
<td>1.423</td>
<td>2.375</td>
<td>2.311</td>
</tr>
</tbody>
</table>
(calculated values are listed in Table 1). This difference was attributed to different atomic structures around the Mn atoms [40]. The local atomic structure of Mn atoms in Ge$_3$Mn$_5$, as given in Ref. [40], is the following: (i) Mn$_1$ neighbors are two Mn$_1$, six Ge and six Mn$_2$ at distances 2.522 Å, 2.534 Å and 3.059 Å respectively; (ii) Mn$_2$ neighbors are two Mn$_2$, four Mn$_3$ and four Mn$_1$ at distances 2.976 Å, 3.051 Å and 3.059 Å respectively. The two Mn atoms nearest-neighbors to Mn$_1$ atoms are at a short distance (2.522 Å) and it was suggested that the interaction with these neighbors would lead to a reduction of the magnetic spin moment of Mn$_1$ atoms. The calculated total spin moment per Mn atom is 2.75μ$_B$, in agreement with previous calculations [34,41,49,50]. This value is slightly higher than the experimental one, i.e. 2.60μ$_B$ [40]. It was shown that a good agreement with experiment is found within GGA and including the spin–orbit interaction into the calculation [34].

The partial density of 3d-states of Mn in Ge$_3$Mn$_5$ is shown in Fig. 3. It is interesting to compare it with the Mn 3d DOS in a diluted magnetic semiconductor Ga$_{1-x}$Mn$_x$As (x=0.125), where Mn atoms substitute Ga. The density of states at the Fermi level in Ge$_3$Mn$_5$ is significant in both spin channels and this compound has a metallic conductivity, as it was found in previous calculations [34].

Because of a strong interaction between Mn atoms, the 3d-bands in Ge$_3$Mn$_5$ are broad. The L$_{2,3}$ spectra reflect electron transitions from the narrow 2p- into the broad valence 3d-bands of Mn, hence the lineshapes in XMCMD spectra at the L$_{2,3}$ edges of Mn in intermetallic compounds is determined by the width of the valence bands. It can be seen from Fig. 3, that the L$_2$ and L$_3$ edges are narrow in Ga$_{1-x}$Mn$_x$As (x=0.125), in agreement with the narrow bands calculated for this DMS.

The resulting XAS and XMCD spectrum, calculated within GGA and HF approximation, are shown in Fig. 4. XAS obtained within both approximations are similar and contain L$_2$ and L$_3$ edges without visible multiplet structure. A large value of the convolution parameter σ = 1 eV in Gaussian functions allows us to reproduce the broad absorption lines found in experimental L$_{2,3}$ spectra of Mn.

The XMCD spectrum contains a fine structure, which can be used to distinguish compounds with different atomic structure around Mn atoms. When all the 3d-states with spin up are occupied, the XMCD spectrum shows a negative A peak and a positive C peak [52]. In solids, the 3d states of Mn are partially occupied and the XMCD spectrum has a more complicated structure: the main absorption line A in the L$_3$ edges is followed by a positive peak B (Fig. 3). This feature of the absorption line is not reproduced by the DFT-GGA calculation [34], however a description of Mn 2p–3d exchange interaction within the HF approximation allows us to obtain a qualitative agreement with experiment. In particular, line B is reproduced, although its intensity is smaller than in experiment (Fig. 4). The intensity ratio between the two absorption edges L$_2$ and L$_3$ is improved as well.

The influence of spin–orbit interaction on the absorption spectrum was studied by solving the Dirac equation for the initial and final states. Then the exchange splitting of Mn 2p sublevels was corrected and the absorption spectrum was calculated according to Eq. (5). The influence of spin–orbit interaction on XAS and XMCD spectrum was found to be small (Fig. 5), and essentially the same spectrum is obtained by solving the Shrödinger equation with spin polarization in MT-spheres.

3.3. The α-Ge$_3$Mn structure

Another structure was initially proposed by Takizawa et al. [53] for Ge$_3$Mn, and further discussed by Arras et al. [28] for α-Ge$_3$Mn as a likely candidate for the crystalline structure of the nanocomposites (Ge,Mn) layers. This structure is derived from cubic Ge, in which the presence of interstitial Mn atoms lowers the formation energy. The formation energy of the α-Ge$_3$Mn was also found

![Fig. 3. 3d-states of Mn in (a) Ge$_3$Mn$_5$, and (c) Ga$_{1-x}$Mn$_x$As (x=0.125). Experimental XMCD spectra at the L$_{2,3}$ edges of Mn in (b) Ge$_3$Mn$_5$ (from Ref. [33]) and (d) Ga$_{1-x}$Mn$_x$As (x=0.084, from Ref. [51]).](image-url)
Within HF approximation.

This metallic compound. The exchange splitting of Mn 2p core levels was evaluated within GGA (dash line) and HF approximation (solid line). Experimental data were taken from Ref. [33].

The L2,3 XMCD spectrum of Mn contains a negative line A, followed by a slightly negative broad line B in the L3 edge. The positive line C at the L2 edge is not symmetric: its left side is sharper that the right one. This asymmetry is due to a splitting of the line C into a more intense C1 and a less intense C2 lines.

The positive line B, observed in the XMCD spectrum of Ge3Mn5, is absent in the spectrum of α-Ge2Mn. The local magnetic moment of Mn in this structure is low (1μB), and the exchange splitting of Mn 2p-states is small. As it was shown in previous section, the line B is reproduced in calculated spectra of Mn if the exchange splitting is properly evaluated, i.e., if the splitting of 2p-states underestimated within GGA, is increased approximately by a factor 2. This suggests that an increase of the local spin moment of Mn, together with the corresponding increase of the exchange splitting, would lead to the appearance of the line B in the XMCD spectrum of α-Ge2Mn.

As a matter of fact, such an increase of the local spin moment of Mn is expected if vacancies are created at the Mn positions in α-Ge2Mn. In particular, in a α-Ge2Mn phase which has the crystal structure of α-Ge2Mn, but only 50% of Mn atoms in their original positions, the local spin moment of Mn is increased to 2.4μB (Table 1). Then line B appears in the theoretical XMCD spectrum (Fig. 7a).

3.4. The C16-Ge2Mn structure

A Ge2Mn phase, related to the α-phases, was proposed in Ref. [27]. This phase has a tetragonal lattice structure with a cell volume smaller than the one in bulk Ge. The calculated spin moment of Mn in C16-Ge2Mn is 1.8μB, that is, larger than the Mn spin moment in α-Ge2Mn (1.0μB). This increased value of the Mn spin moment enhances the exchange splitting of the 2p-core states (Fig. 2).

Different band structures in the α- and C16-phases, as well as different values of the 2p-levels exchange splitting, cause differences in their XMCD spectra. The line B in the XMCD spectrum of C16-Ge2Mn contains a negative part, which is followed by a positive one (Fig. 7b). This unusual behavior of the line B may be used to identify the C16-Ge2Mn phase.

3.5. Ge3Mn and Ge4Mn with diamond structure

We now consider Ge with the usual diamond structure, where Mn atoms are located in substitutional or interstitial positions. The Mn concentrations were taken to be 25% for substitutional Mn (i.e., Ge3Mn) and 20% for interstitial Mn (i.e., Ge4Mn). These compositions are within the range experimentally observed in different Mn-rich (Ge,Mn) phases [22,26,54].
3.6. Discussion

We have shown that more accurate simulations of the XMCD spectra can be achieved using the precise calculation of the core levels splitting. This correct splitting can be obtained from the eigenvalues of initial 2p-states, calculated within the HF approximation and under the assumption of a weak screening of the exchange interaction between the 2p- and 3d-electrons. The validity of the latter is confirmed by our results. The final valence states can be still described within DFT, since the DFT eigenvalues in metals are rather close to quasiparticle energies.

One can note that many-body effects, such as relaxation of the electron system after excitation [55], and the mixing of L2 and L3 edges due to Coulomb interaction between electrons of Mn [56], are not taken into account in this calculation and may modify the XMCD spectrum. In addition, the influence of defects on the electronic state of Mn should be also taken into account when a comparison to experimental spectra is done, as well as the disordered structures in the nanocolumn samples, which contain Mn in the nanocolumns but also in the matrix and at the interface. All these factors make it difficult to use XMCD spectra for the determination of the crystal structures of metallic compounds.

However, we have shown that the more accurate simulation of the XMCD spectra using the precise calculation of the core levels splitting reveals details on the XMCD spectra lineshape (e.g. the presence or absence of the positive peak labeled B at about 643 eV) that were up to now eluded in standard calculations.

4. Summary and conclusions

XAS and XMCD spectra at the L2,3 edges of Mn in different (Ge,Mn) compounds were calculated from first principles. Early calculations show that DFT-based calculations are not able to reproduce some features in the XMCD spectra of Mn. In particular, the positive part of the L3 edges of Mn in Ge3Mn is absent in the calculated XMCD spectrum, while it is observed in experiment. In this work we show that this positive part can be reproduced if the core levels splitting is accurately calculated, in agreement with previous results [36,37]. The effect of spin–orbit interaction between valence electrons was also considered and found to be small.

(Ge,Mn) compounds with a large Mn content usually feature a metallic character. The XAS of such metallic compounds are broad and have no particularities which can help to identify different compounds. XMCD spectra have a more detailed structure and their shape depends on the local spin moment of Mn and the crystal structure. In this work we have compared XMCD spectra calculated for two energetically stable phases of (Ge,Mn), with those calculated for substitutional and interstitial Mn in Ge. The XMCD spectra of all the (Ge,Mn) phases have a similar structure and shape, but also small peculiar features which may be used to identify a particular (Ge,Mn) compound.

The method to improve the agreement between theoretical and experimental XMCD spectra that we suggest in this paper can easily be applied to other systems of interest, such as for example transition metal impurities on surfaces where a similar change of sign after the main L3 peak has been observed in the experimental XMCD spectra [57], or other homogeneous transition metal compounds.
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