Invited Review

Hard x-ray emission spectroscopy: a powerful tool for the characterization of magnetic semiconductors

M Rovezzi and P Glatzel

European Synchrotron Radiation Facility, 6 rue Jules Horowitz, F-38043 Grenoble, France
E-mail: mauro.rovezzi@esrf.eu

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Abstract
This review aims to introduce the x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS) techniques to the materials scientist working with magnetic semiconductors (e.g. semiconductors doped with 3d transition metals) for applications in the field of spin-electronics. We focus our attention on the hard part of the x-ray spectrum (above 3 keV) in order to demonstrate a powerful element- and orbital-selective characterization tool in the study of bulk electronic structure. XES and RIXS are photon-in/photon-out second order optical processes described by the Kramers–Heisenberg formula. Nowadays, the availability of third generation synchrotron radiation sources permits applying such techniques also to dilute materials, opening the way for a detailed atomic characterization of impurity-driven materials. We present the Kβ XES as a tool to study the occupied valence states (directly, via valence-to-core transitions) and to probe the local spin angular momentum (indirectly, via intra-atomic exchange interaction). The spin sensitivity is employed, in turn, to study the spin-polarized unoccupied states. Finally, the combination of RIXS with magnetic circular dichroism extends the possibilities of standard magnetic characterization tools.

Keywords: magnetic semiconductors characterization, x-ray emission spectroscopy, resonant inelastic x-ray scattering, spintronics, synchrotron radiation

(Some figures may appear in colour only in the online journal)

1. Introduction

Semiconductors doped with few per cent (10²⁰–10²¹ at cm⁻³) of magnetic elements such as transition metals (TMs) or rare earth elements (RE) are promising building blocks for semiconductor-based spin-electronics [1, 2] (spintronics). In the dilute magnetic semiconductors (DMSs) model, the TM (RE) dopants randomly substitute in the host semiconductor and, due to the unpaired d(f) states, bring a local net magnetic moment. These local moments, via interatomic exchange interactions (eventually mediated by defects or carriers), bring magnetic properties to the semiconductor, leading to an overall half-metallic behavior [3], that is, the presence of spin polarization at the Fermi level. Such materials can be used then as injector or detector for spin-polarized currents in semiconductors and permit realising spintronics devices such as, for example, the proposed spin field-effect transistor [4], overcoming the conductivity mismatch problem [5] that arises for ferromagnetic-metal/semiconductor heterostructures. It is important to clarify that non-magnetic semiconductors such as II–VI or III–V alloys (e.g. GaAs, GaN or ZnO) have been identified historically as host materials for DMSs, because their epitaxial growth is of high quality and they can be easily integrated in CMOS technology (which is currently used for constructing integrated circuits). Recently, pushed by the advances in epitaxial growth of oxide materials [6, 7], bulk magnetic oxides such as TM oxides are also considered for semiconductor spintronics. We will
focus mainly on DMSs because these materials represent an ideal workbench for testing new and exciting effects such as quantum spintronics [8–10] (also known as solotronics) or the spin solar cell [11, 12] and others [13].

DMSs currently suffer from low (ferro)magnetic transition temperatures. In order to obtain magnetic coupling persisting well above room temperature, the concentration of the active dopants is pushed (in most cases) far above the thermodynamic solubility limit by out-of-equilibrium epitaxial growth methods (e.g. low temperature molecular beam epitaxy). This can cause side effects such as the incorporation of counter-productive defects (e.g. Mn interstitials in Ga1-xMnx) or a chemical phase separation, where the density of the magnetic impurities is not constant over the host crystal (condensed magnetic semiconductors, CMS). Two recent reviews [14, 15] describe in detail the status of current research on DMS/CMS both from the experimental and theoretical point of view, respectively. They show a growing consensus that theoretical results can drive the experiments in the optimization of new and exciting materials only if an accurate characterization at the nano-scale and at bulk level is put in place [16].

In order to tackle this point, we review a spectroscopic technique, the hard x-ray emission spectroscopy (XES) with synchrotron radiation (resonant inelastic x-ray scattering, RIXS) that is a powerful tool in characterizing such materials. It is a direct feedback for the scientists who need to engineer their materials at the nano-scale (bottom-up approach) via a fine control of their atomic and electronic structure. This permits the realization of relevant devices and to explore new ideas and concepts in spintronics. The application of RIXS to doped semiconductors is stimulating also for the theoreticians aiming to calculate experimental (spectroscopic) observables. In fact, RIXS permits combining two theoretical approaches to the description of the electronic structure of matter: band calculations based on the density functional theory (DFT) and atomic calculations based on the ligand field multiplet theory (LFMT). In fact, on one hand, DMSs are well described by atomic calculations based on the ligand field multiplet theory (LFMT), in (extended x-ray absorption fine structure) techniques [17], described by the multiple scattering theory [18], permit extraction of the local geometry/symmetry and the bond distances, plus the coordination numbers and disorder from the analysis of the fine structure. XANES and EXAFS have been successfully applied to the geometric structure analysis in semiconductor heterostructures [19], DMS/CMS [20, 21] and low-dimensional systems [22].

XAS can be used also as an element-selective magnetometer by recording the difference in absorption of linearly/circularly polarized light in the presence of a magnetic field, the x-ray magnetic linear/circular dichroism (XMLD/XMCD) technique [23]. This is an advantage with respect to those techniques where the whole sample response to an external perturbation is measured (e.g. superconducting quantum interference device magnetometry [24] or electron paramagnetic resonance [25]). With respect to DMS/CMS, XMCD was successfully combined with the x-ray (natural) linear dichroism [26] (XLD) and systematically applied to the study of Zn1−xO to link the local magnetic and structural properties [27]. For 3d TM, XMCD is usually measured at the L edges, residing in the soft x-ray region (below 1 keV) or at the K edges, residing in the hard part of the spectrum (above 3 keV). XMCD at the L edge has the advantage of accessing the partially filled d orbitals via direct electric dipole transitions and the possibility to separate the spin and orbital contribution to the magnetic moment via sum rules [28, 29]. XMCD at the K edge probes only the orbital component and results in a very small signal (≈10−3 times smaller that XLD). The advantages in using hard x-rays consist in the sample environment and the bulk sensitivity. A vacuum environment around the sample is not required with hard x-rays, thus it is possible to measure in operando devices or in extreme conditions (e.g. high pressure). Furthermore, the higher penetration depth permits probing bulk properties and accessing buried interfaces or superstructures (e.g. two-dimensional electron/hole gases) that are the relevant structures of real devices to study spin transport mechanisms. Soft x-rays are suitable in the case of thin films (few tens of nm thick) deposited on a substrate, where the electron yield (EY) detection is used as surface probe, and the fluorescence yield (FY) as representative of the full thickness. Nevertheless, FY suffers from strong self-absorption effects and is not a true measurement of the linear absorption coefficient as obtained in transmission measurements or EY [30, 31]. This has relevant consequences on the study of magnetic materials with soft x-rays XMCD because it means...
that it is not possible to compare EY measurements to FY ones and, most importantly, it implies the non-applicability of sum rules. An alternative method based on x-ray emission has been proposed recently [32, 33]. To overcome those difficulties, the use of a hard x-ray probe in an inelastic scattering configuration is gaining momentum. By working in an energy loss scheme (inelastic scattering) it is possible to reach the same final states reachable with soft x-rays in a second-order process, that is, by passing via an intermediate state that is excited resonantly, strongly enhancing the spectral features [34].

With respect to XAS, in this review we focus on the low-energy range of the K edge, the pre-edge features [35–37]. These features are enhanced by collecting the fluorescence channel across the absorption edge with a small energy bandwidth, as obtained via a wavelength dispersive spectrometer (WDS). This technique is nowadays referred to as high-energy resolution fluorescence detected (HERFD) XAS [38]. The acronym RIXS here includes resonant x-ray emission spectroscopy (RXES), that is, the direct RIXS of [39] or the spectator RXES of [40]. In addition, the initial and intermediate core hole states are also reported for clarity. The RIXS done by collecting the Ko1 emission line is denoted as 1s2p3/2 RIXS. We refer then to XES as the FY measured after photoionization and scanned via a WDS. The presentation of XES and RIXS follows previous reviews [38, 41–45] by extending the applicability to magnetic semiconductors. The specific case of non-resonant inelastic x-ray scattering [46], the x-ray Raman scattering (XRS), is not treated here. XRS permits measurement of the K-edge of light elements (e.g. C, N, O) with hard x-rays [47, 48]. A possible application of XRS is the study of doping mechanisms with shallow impurities (such as the case of co-doping in magnetic semiconductors), but it is currently not applicable to dilute systems. The very low cross section limits the application of XRS. XES and RIXS are also extensively employed in the soft x-ray energy range [39, 49, 50]. One relevant application is the element-selective mapping of the valence and conduction bands [51, 52]. RIXS is also often used to study collective excitations in systems with long-range order. The analysis of the energy dispersion as a function of the momentum transfer permitted identifying a two-directional modulation in the charge density dispersion as a function of the momentum transfer permitted in systems with long-range order. The analysis of the energy bandwidth, as obtained via a wavelength dispersive fluorescence channel across the absorption edge with a small range [39, 49, 50]. One relevant application is the element-selective mapping of the valence and conduction bands [51, 52]. RIXS is also often used to study collective excitations in systems with long-range order. The analysis of the energy dispersion as a function of the momentum transfer permitted identifying a two-directional modulation in the charge density dispersion as a function of the momentum transfer permitted.

2. Kramers–Heisenberg formalism

We present in the following a brief introduction to the theory of XES. A more comprehensive treatment of the theory is available in recent review papers and books: Gel’man and Ågren [49, 56] (molecules), de Groot and Kotani [57] (hard and soft x-rays in condensed matter), Rueff and Shulka [46] (high pressure applications) and Ament et al [39] (elementary excitations in solid state physics). X-ray emission is a secondary process that occurs after creation of a vacancy in an inner-shell of the element of interest. In most applications this vacancy is created after photoexcitation and x-ray emission becomes a photon-in/photon-out process and therefore an x-ray scattering phenomenon. Alternatives to photoexcitation exist (e.g. ion or electron bombardment, radioactive isotopes) but the theoretical treatment in these cases only requires minor adjustments with respect to the following considerations. In the general description of a scattering process (see figure 1 for the scattering geometry), a photon of energy hωin, wave vector k_in, and unit polarization vector ε_in is scattered by the sample with ground state eigenfunction |g⟩. A photon is emitted into a solid angle dΩ described by a polar angle θ and azimuthal angle φ. The scattered photon has energy hωout, wave vector k_out and polarization ε_out. The energy hω = h(ω_in−ω_out) and momentum hq = h(k_in−k_out) are transferred to the sample that consequently makes a transition from the ground state |g⟩ with energy E_g to the final state |f⟩ with energy E_f. The derivation of the double differential scattering cross section, d²σ/(dΩdhωout), by means of second-order
perturbation treatment can be found in many textbooks (e.g. Schülke [58] and Sakurai [59]). The x-ray electromagnetic field is represented by its vector potential $A$. By neglecting the interaction of the magnetic field with the electron spin, the interaction Hamiltonian is written (in SI units) as \[ H_{\text{int}} = \frac{e^2}{2m} \sum_j A(r_j)^2 + \frac{e}{m} \sum_j p_j \cdot A(r_j) \] (1)

where $p_j$ is the momentum of the $j$th target electron. The transition probability is given by the golden rule $\langle \sigma_2 | T | s_1 \rangle$ where $T$ is a transition operator connecting two eigenstates. The term containing $A^2$ does not involve the creation of a hole in a core level of the element of interest. As in example, for Mn this would be the levels $1s$, $2s$, $3s$, $3p$ (cf figure 2). We refer to the resonant term as the Kramers–Heisenberg cross section. This term governs x-ray absorption (when considered as coherent elastic forward scattering) and x-ray emission including all resonant scattering processes. The interaction terms can be treated separately, assuming implicitly that the experimental conditions are chosen such that one term dominates. Other terms and interference with them are not taken into account. Removing unimportant factors, the essential part of the RIXS spectrum can be described in the following form [58]

\[ \sigma(\omega_{\text{in}}, \omega_{\text{out}}) = r_c^4 \sum_n \sum_f \left( \frac{\Gamma_{\text{out}}}{\omega_{\text{in}} - \hbar \omega_{\text{in}} - \Gamma_{\text{out}}^2/4} \right)^2 \times \delta(E_{\text{in}} - E_f + \hbar \omega_{\text{out}} - \hbar \omega_{\text{out}}) \] (2)

where $r_c$ is the classical electron radius and $T$ the transition operators $T = \sum_j (\epsilon \cdot p_j) e^{i k \cdot r_j}$. $\Gamma_n$ denotes the spectral broadening due to the core hole lifetime of the intermediate state $|n\rangle$ as a result of the Auger and radiative decays of the core hole. The lifetime is often assumed constant for a given subshell core hole. In order to account for the finite lifetime of the final states, the energy-conservation $\delta$-function can be broadened into a Lorentzian of full width at half maximum $\Gamma_f: \Gamma_f = \hbar \omega_{\text{in}} / \hbar \omega_{\text{out}} = \Gamma_{\text{out}}^2/4$. A final approximation that is employed for practical calculation of the Kramers–Heisenberg cross section is the expansion to the second order of the transition operators. This leads to $T \approx \epsilon + \frac{1}{2} (\epsilon \cdot r)(k \cdot r)$ and corresponds to a description of the cross section in terms of dipole (E1) and quadrupole (E2) transitions only.

### 2.1. Kramers–Heisenberg equation for XES

The Kramers–Heisenberg equation (equation (2)) is the basis for x-ray absorption and emission spectroscopy. We note that this view is at odds with some publications where the Kramers–Heisenberg equation is only applied to excitations just above ($\approx 0\text{–}20 \text{ eV}$) the Fermi level. Such excitations are referred to as resonances. However, x-ray emission after photoionization also has to be treated using the formalism of equation (2) and there is no fundamental difference between excitations close to or well above the Fermi level. Interference effects may be more likely to be important just above an absorption edge but this does not suffice for a clear distinction.

The cross section changes dramatically within the first tens of eV above an absorption edge and an approach similar to $\Gamma_f$ dependence. In this range, the photoelectron (described by its energy $\epsilon$) does not interact with the remaining ion; the intermediate and final states with their energies are written as \[ |n\rangle = |n\rangle |\epsilon\rangle, E_n = E_{\text{in}} + \epsilon \text{ and } |f\rangle = |f\rangle |\epsilon\rangle, E_f = E_{\text{in}} + \epsilon \] (cf figure 3). The photoelectron does not change its energy upon the radiative decay of the ion. One thus obtains, for each ionic intermediate and final state, $n'$ and $f'$, an infinite number of states characterized by the kinetic energy of the photoelectron. Equation (2) then becomes

\[ \sigma(\omega_{\text{in}}, \omega_{\text{out}}) \propto \sum_n \sum_f \frac{\langle f | \langle T_{\text{out}} | \epsilon \rangle | n' \rangle \langle n' | \langle T_{\text{in}} | \epsilon \rangle | f \rangle \rangle^2}{\Gamma_f / 2 \pi} \]

\[ \Gamma_f = \sqrt{\Gamma_{\text{out}}^2 / 4 + 2 \pi \omega_{\text{in}} / \hbar} \] (3)
Figure 3. Simplified total energy diagram for XES. A continuum of intermediate states is reached whose energies depend on the photoelectron kinetic energy $\varepsilon$. Several of these pairs of states may exist (with different $n'$, $f'$ and $\varepsilon$) that need to summed up for a full treatment of the x-ray emission process after photo excitation.

We assume constant absorption and emission matrix elements for each $n'$, $f'$, i.e., independent of the photoelectron kinetic energy $\varepsilon$ (which is justified over a small energy range), and we obtain

$$
\sigma(\varepsilon_{\text{in}}, \varepsilon_{\text{out}}) \propto \sum_{f''} \sum_{n''} \left| \langle f' | T_{\text{out}}^{n'} | \varepsilon \rangle \langle n'' | T_{\text{in}}^{f'} | \varepsilon \rangle \right|^2
\times \int \frac{1}{\Gamma_2/2\pi} \frac{(E_{f''} - (E_{f'} + \varepsilon) + \hbar \varepsilon_{\text{in}})^2 + \Gamma_{\varepsilon}^2/4}{(E_{f''} - (E_{f'} + \varepsilon) + \hbar \varepsilon_{\text{in}} - \hbar \varepsilon_{\text{out}})^2 + \Gamma_{\varepsilon}^2/4}.
$$

The integral over $\varepsilon$ is a convolution of two Lorentzian functions which gives a Lorentzian as a function of $\varepsilon_{\text{out}}$ with width $\Gamma_{\varepsilon}$ which is the known result for non-resonant fluorescence spectroscopy. A broad energy bandwidth for the incident beam will result in a larger range of photoelectron kinetic energy but not influence the width of the convoluted Lorentzian. Hence, the spectral broadening is independent of the incident energy bandwidth. This opens the door to experiments using non-monochromatic radiation with a bandwidth of $\Delta E < 100$ eV (pink beam) at synchrotron radiation sources or free electron lasers [61].

The spectral shape does not depend on $\varepsilon$ as long as the same set of intermediate states $n'$ is reached. This may change if the incident energy suffices to create more than one core hole (see [62] and references therein). One example is the KL-edge where one incident photon creates a hole in the K- and L-shell. This may significantly alter the x-ray emission spectral shape. It is therefore important to choose the incident energy below the edge of multi-electron excitations, if possible.

3. Approaches to the calculations

In this section we will present a short overview of the methods currently employed to calculate the experimental spectra. The theoretical simulation is an important tool for the experimentalist who needs to analyze the collected spectra and to plan new experiments. We can roughly separate the various approaches to the calculations of inner-shell spectra into two main philosophies, that we can refer to as: many-body atomic picture and single-particle extended picture. They are based, respectively, on LFMT and DFT.

In LFMT, one first considers a single ion and writes its wavefunction as a single or linear combination of Slater determinants of atomic one-electron wavefunctions. The chemical environment is then considered by empirically introducing the crystal field splittings and the orbital mixing. A detailed description of LFMT can be found in textbooks [57, 63, 64] or topical reviews [41, 65, 66], while a tutorial-oriented description of the calculations was given by van der Laan [67]. The codes currently in use are those developed by Cowan [68, 69] in the sixties and extended by Thole in the 1980s (see [70] for a technical overview). Recently, a user friendly interface, CTM4XAS [71], has permitted a larger community to access such calculations. The advantage of this approach is that the core hole is explicitly taken into account and multi-electron effects are calculated naturally by applying multiplet theory. The obvious problem with this approach is that the chemical environment is only considered empirically.

In the DFT-based approach, a simplified version of the Schrödinger equation is solved either for a cluster of atoms centered around the absorbing one (real space method) or using periodic boundary conditions (reciprocal space method). This means that the electronic structure is calculated ab initio, without the need of empirical parameters, and the results depend on the level of approximation employed. Among the large number of presently used codes, the most common techniques are: multiple scattering theory (e.g. EMT9 [72, 73], DMNES [74, 75] and MXAN [76]), full potential linearized augmented plane wave, FLAPW (e.g. WEN2K [77, 78]), projector augmented-wave method, PAW (e.g. QUANTUM-ESPRESSO [79–81], GPAW [82, 83], BIGDFT [84]) and time-dependent DFT (e.g. ORCA [85, 86]). The advantage in the DFT approach is that the theoretical framework is well established and numerous groups work on evaluating and improving the level of theory, i.e., the exchange-correlation functionals or the basis sets. However, DFT is a theory to calculate the ground state electronic structure which is a priori incompatible with inner-shell spectroscopy. Furthermore, in its basic implementation, DFT calculates one-electron transitions which are insufficient when the inner-shell vacancy gives a pronounced perturbation of the electronic structure, resulting in important many-body effects. These shortcomings have been addressed within DFT and considerable progress has been made [87].

The decision on which approach is most suitable for the problem at hand can be based on the degree of localization of the orbitals that are assumed to be involved in the transitions. The K absorption main edge in 3d TMs is often modeled using DFT. The pre-edge requires a mixture of atomic and extended view and therefore only in a few favorable cases has a good understanding of the pre-edge features been achieved. The L-edges of rare earths and 5d TMs require an extended
approach. However, 2p to 4f transitions that form the L pre-edge in rare earths are highly localized and an atomic approach is very successful. The Kβ main line emission in 3d TMs involves atomic orbitals. Multilevel theory can therefore reproduce the spectral shape to high accuracy. In contrast, the VTC lines involve molecular orbitals that are mainly localized on the ligands and a one-electron DFT approach is therefore very successful in reproducing the spectra.

It is often illuminating to apply a very simplified approach to simulate an experimental result, as it permits assessing what interactions and effects are relevant. As an example, if one neglects interference effects, the core hole potential and multi-electron transitions, it is possible to drastically simplify the Kramers–Heisenberg formula (equation (2)) for the case of VTC RIXS and obtain an expression in terms of the angular momentum projected density of states

\[
\sigma (\omega_{\text{in}}, \omega_{\text{out}}) \propto \int \rho(\varepsilon) \rho'(\varepsilon + \omega_{\text{in}} - \omega_{\text{out}}) \left( \varepsilon - \omega_{\text{out}} \right)^2 + \Gamma_n / 4 \] (5)

where \(\rho\) and \(\rho'\) are, respectively, the occupied and unoccupied density of states, \(\Gamma_n\) the lifetime broadening of the intermediate state. This approach has been demonstrated to be valid in describing the VTC-RIXS spectra of 5d TM systems [89, 90]. A similar approach but partly considering the core hole potential and the radial matrix element was recently implemented in the FEFF9 code [91].

The combination of an extended picture with full multiplet calculations is the holy grail in theoretical inner-shell spectroscopy. The progress in recent years has been impressive to the great benefit of the experimentalists who are gradually getting a handle on analyzing their data [92–94]. A promising method is to make use of maximally localized Wannier functions [95] as directly obtained from DFT calculations. If one extracts the Wannier orbitals in the bands near the Fermi level, it is then possible to calculate the spectra via LFMT [96]. However, this method is still an approximate solution of the problem. A more rigorous treatment was proposed in the framework of the multi-channel multiple scattering (MCMS) theory [97] (recently revised in [98]). The MCMS method has been successfully applied in simulating the L_{2,3} XAS spectra of Ca [99] and Ti [100] and could be easily extended to XES and RIXS.

4. Experimental set-up

Before presenting a selection of applications of the technique, we describe how a combined XAS/XES experiment is performed on a generic synchrotron radiation beamline. This is schematically illustrated in figure 4. The synchrotron radiation is produced in the storage ring via an undulator, bending magnet or wiggler (source). A first collimating mirror, run in total reflection geometry, is usually used to reduce the heat load, collimate the beam and remove the higher harmonics. The beam is then monochromatized by a double single crystal monochromator (cryogenically cooled); typically two pairs of crystals are employed: Si(111) or Si(311), giving an intrinsic power, \(\frac{\gamma}{\Delta \varepsilon}\), of 7092 and 34 483 [101], respectively. The monochromatic beam is then focused to the sample via a focusing system, typically, two bent mirrors in Kirkpatrick–Baez geometry [102], that is, working in glancing incidence (around 3 mrad), one focusing horizontally and the second one, perpendicular to the previous, focusing vertically. A given number of slits (vertical and horizontal) is also inserted in the beam path to clean for aberrations and reduce the divergence. In addition, the beamline optics can be complemented with a second monochromator or phase retarders. The second monochromator, typically a channel cut in four crystals configuration [103], is used to improve the energy resolution. The phase retarders [104], typically thin diamond crystals put in diffraction conditions, permit tuning the polarization of the x-ray beam. In fact, apart from helical undulators, the x-ray beam is linearly polarized in the orbital plane and the phase retarders are required for generating circularly polarized light (left and right) or linearly polarized in the vertical plane.

In the experimental station, the equipment is built around the sample stage (figure 4). The main elements consist in x-ray detectors for monitoring the incoming and transmitted beam and measuring the fluorescence emitted by the excited...
sample. For hard x-rays, the sample environment does not require a vacuum chamber and it is quite versatile: a goniometer permits aligning the sample in three dimensions plus hosting additional equipment (e.g. crystal, furnace, magnet or chemical reactor). For bulk samples, the XAS (absorption coefficient, $\mu(\hbar\omega_{in})$) is measured directly via the intensity of the incoming ($I_{in}$) and transmitted beam ($I_{out}$), according to the Beer–Lambert law: $I_{out} = I_{in}e^{-\mu(\hbar\omega_{in})}$, where $x$ is the sample’s thickness. For dilute species, $\mu$ cannot be measured directly and a secondary process (yield) has to be employed, assuming that the absorption cross section is proportional to the number of core holes created. The secondary processes can be either the collection of the EY [105] or the FY [106]. We will not treat the FY here, but focus on the FY because this gives access to a photon-in/photon-out spectroscopy, as XES and RIXS. Usually, the FY-XAS is collected either without energy resolution (total FY) or with an energy dispersive solid state detector (SSD) as an array of high purity germanium elements or silicon drift diodes. For linearly polarized synchrotron radiation (with $e_{\alpha}$ along $x$, see figure 1, as in standard experiments) the Thomson (elastic), Compton and Raman (inelastic) scattering have an angular dependence of $\sin^2(\phi) + \cos^2(\theta) \cos^2(\phi)$ (see figure 1) while the fluorescence emitted by the sample is isotropic (in a standard geometry and not considering polarization effects, see [107] for the full expression), thus the fluorescence detectors are usually put at 90° on the polarization plane to minimize the background due to scattering (see figure 4). SSD detectors permit a typical energy resolution of 150–300 eV ($E/\Delta E \approx 50$). This low energy resolution combined with a low saturation threshold is a drawback for measuring dilute species in strong absorbing matrices as DMS/CMS. In fact, the weak signal of interest is very often sitting on the strong background coming from the low-energy tail of the Thomson and Compton scattering or overlapping with the fluorescence lines of the other elements contained in the matrix. For thin films deposited on a substrate, a workaround for collecting a clean fluorescence signal is to work in a combined grazing incidence and grazing exit geometry [108] but this has the drawback of fixing the experimental geometry and it is not suitable for single crystals where it is important also to work with the polarization axis laying out of the sample surface. An increased energy resolution ($E/\Delta E \approx 1000$) can be obtained with charged coupled devices [109] or microcalorimetric arrays [110] used in energy resolving mode. However, the complexity of these detectors (especially in the events reconstruction algorithms) and the very quick saturation for calorimeters, limits their application on standard spectroscopy beamlines.

In order to overcome these limitations and to collect XES, RIXS and HERFD-XAS, a WDS has to be employed ($E/\Delta E > 5000$). For hard x-rays, this means that Bragg’s diffraction over an analyzer crystal is employed to monochromatize the emitted fluorescence from the sample (Rowland’s circle geometry). Among all the possible diffraction geometries [111], two main configurations are currently in use at synchrotron facilities: the point-to-point Johann [112] and the dispersive Hamos [113]. For both, the basic principle is that the source (sample), the diffractor (analyzer crystal) and the image (detector) are on the Rowland circle. The first class uses spherically bent crystals [114] in combination with one-dimension detector; the energy selection is performed by scanning the crystal Bragg’s angle and the detector over the Rowland circle. In the second class, a cylindrically bent crystal is combined with a position-sensitive detector; the energy dispersion is obtained without moving the crystal and by collecting the different areas of the detector. Without going into the details of the advantages and disadvantages of each configuration, good performances are obtained with an increased number of spherically bent crystals (to overcome the small solid angle collected, $\approx 0.03$ sr per crystal) working at Bragg’s angles close to 90°. As a few examples of currently available instruments, there are those dedicated to XRS [115, 116], medium-resolution RIXS [43, 117–119] and single-shot XES [120, 121].

5. The RIXS plane and sharpening effects

An experimental 1s2p RIXS intensity plane is shown in figure 5 in the incident ($\hbar\omega_{in}$) versus transfer ($\hbar\omega_{in} - \hbar\omega_{out}$) energy axis. The transitions to continuum (main absorption edge) appear as dispersive features along the diagonal, while the transitions to localized states (pre-edge features) appear as resonances at well defined positions in the plane. The two groups of diagonal features visible in figure 5 are vertically split by the 2p spin–orbit interaction in the final state, corresponding to the $K\sigma_1$ and $K\alpha_2$ emission lines. A diagonal cut (constant emitted energy, CEE) will then give the HERFD-XAS spectrum, while an integration over the vertical direction results in a standard XANES spectrum. Considering only the pre-edge region, a vertical cut (constant incident energy, CIE) gives a spectrum sensitive to the spin–orbit interaction in the final state and the exchange interaction between the intermediate and final states. This is similar to $L_{2,3}$ edges XAS. A cut in the horizontal direction (constant final state energy, CFS) is affected by the spin–orbit and exchange interaction in the intermediate state only. On the other hand, analyzing RIXS data as line scans can lead to false interpretation of the spectral features. For example, the two pre-edge peaks in figure 5 have an incoming energy separation of 1.8 eV that would be underestimated (1.4 eV) if a peak-fitting procedure is employed on the HERFD-XAS scan. This is due to the fact the first resonance does not lie on the diagonal of the RIXS plane (see figure 5).

One appreciated feature of RIXS/HERFD-XAS is a dramatic improvement in resolving the spectral features (sharpening effect). The effect is striking at the $L_{2,3}$ edges of 5d elements when compared to standard XANES while at K pre-edge of 3d elements permits catching fine details due to the strong reduction of the background signal. For example, HERFD-XAS has permitted to precisely follow catalytic reactions [123] or to reveal angular-dependent core hole effects [124]. The origin of the sharpening effect was attributed to interference causing the elimination of the core hole broadening [125]. Actually, the interference does not play a role here and the lifetime broadenings are still present, as shown by the elongated features in the horizontal and vertical direction of the RIXS plane (see figure 5). Without going into the details of the difference between HERFD-XAS and...
standard XAS spectra, as previously discussed by Carra et al [34], it was demonstrated that the improved resolution of the experimental spectra can be reproduced by an apparent broadening [126]

\[ \Gamma_{\text{exp}} \approx \frac{1}{\sqrt{(1/\Gamma_n)^2 + (1/\Gamma_f)^2}} \] (6)

where the intermediate (\(\Gamma_n\)) and final (\(\Gamma_f\)) core hole lifetime broadenings are taken into account.

6. Valence states sensitivity of K fluorescence lines

The macroscopic properties of semiconductors (e.g. transport, magnetism) are driven by impurities (defects) located at valence states. Accessing the information of such states via a bulk probe, permits then having a detailed description of the material under study. XES can probe valence electrons either indirectly or directly, by selecting the yield for different transitions. If one collects CTC transitions, the valence electrons are probed indirectly, and directly for VTC. The selectivity to the electronic structure of the valence shell in CTCXES originates from screening effects (the core levels energy is affected by the modified nuclear potential) and multiplet structure (the spin and orbital angular momentum of the core hole strongly couple to the valence electrons). The screening dominates for light elements such as, for example, the K\(\alpha\) XES of S [127], while the multiplet structure dominates in the case of the K fluorescence lines of 3d TMs.

An XES spectrum is given in figure 6 for Cr in Cr\(_2\)O\(_3\). The most intense lines are the K\(\alpha_1\) (K-L\(_3\), 2p\(_{1/2}\) \(\rightarrow\) 1s) and K\(\alpha_2\) (K-L\(_2\), 2p\(_{1/2}\) \(\rightarrow\) 1s), where the 2p level is split by the strong spin–orbit interaction. With \(\approx\)10-times smaller intensity are visible the CTC-K\(\beta\) lines (K-M\(_2\), 3p \(\rightarrow\) 1s), called [128] K\(\beta\)\(_{1,3}\) (main peak) and K\(\beta\)' (broad shoulder at lower emitted energy). Finally, the VTC-K\(\beta\) lines appear on the tail of the main lines with roughly 200-times smaller intensity, those are called K\(\beta\)\(_{2,5}\) and K\(\beta\)". The origin and information content of CTC-K\(\beta\) lines is given later in section 7, while here we focus first on VTC-K\(\beta\) lines.

The VTC-K\(\beta\) arises from transitions from occupied orbitals a few eV below the Fermi level (the valence band), that is, from orbital mixed metal–ligand states of metal \(p\)-character to 1s. For this reason, VTC-K\(\beta\) is strongly sensitive to ligand species and has been employed in chemistry to distinguish between ligands of light elements [129–132] (e.g. C, N, O, S). In addition, by making use of the XES polarization dependence [42] it is possible to study the orientation of the ligands. For example, Bergmann et al [133] studied a Mn nitrido coordination complex in \(C_4v\) symmetry with 5 CN and 1 N ligand at a very short distance (1.5 Å). The signal arising from the nitrido molecular orbitals was almost completely suppressed by orienting the Mn-nitrido bond in the direction of \(k_\text{out}\), i.e., toward the crystal analyzer. Another advantage of VTC-K\(\beta\) is the possibility to easily calculate the transitions with a molecular-orbital approach: from early atomic [134] to recent DFT methods [135–137]. These works demonstrate that the K\(\beta\)" and K\(\beta\)\(_{2,5}\) are mainly sensitive, respectively, to the ligand \(s\) and \(p\) states. The K\(\beta\)\(_{2,5}\) has also a strong dependence on the metal’s local symmetry [138, 139] (e.g. \(T_D\) versus \(O_h\)). For a more rigorous treatment, the interested reader can refer to a recent topical review [140].
In DMSs, one application of VTC-Kβ is in the study of the interaction of shallow dopants with the metal site. For example, in Zn1−xCr,Te co-doped with N [141], where N is an acceptor (brings holes in the valence band), by measuring the Cr VTC-Kβ it is possible to detect when N interacts with Cr via the clear signature of N 2s levels in the Cr Kβ′′. This is illustrated in figure 7 where we show a selection of VTC-Kβ spectra for commercially available Cr-based powder compounds compared with the \textit{ab initio} simulations (FDMNES code [75]). Standard crystal structures (retrieved from the ‘Inorganic Crystal Structure Database’, FIZ Karlsruhe) are used as input in the calculations, conducted in real space with a muffin-tin approximation and the Hedin–Lundqvist exchange-correlation potential. To compare with the experiment, the calculated Fermi levels are arbitrarily shifted and the spectra are convoluted with a constant Lorentzian broadening of 2.68 eV. The origin of the features is then attributed by selecting the projected density of states on the ligands that overlaps with the metal p one (not shown). This confirms previous works, that is, the Kβ′′ mainly comes from the ligand s states, while the Kβ′′ is from the ligand p states. As shown in figure 7, the energy position of the Kβ′′ is very sensitive to the type of ligand and permits identifying if a compound has an additional phase. For example, the experimental Cr2Te3 spectrum shows a second Kβ′′ at 5967 eV, corresponding to oxygen, that is not reproduced in the calculation. The origin of this extra feature is then easily understood by the fact that Cr2Te3 is an air-sensitive compound and, due to the measurements carried in air, it was contaminated by oxygen. The analysis of the Kβ′′ is more demanding, because its spectral features are also affected by the local symmetry. This effect is also shown in figure 7, where the simulated and experimental Kβ′′ do not fully align. One reason resides in the fact that the simulation takes into account only one crystallographic structure, while the commercial powders may contain more than one crystal phase of the same compound.

7. Kβ spin sensitivity via intra-atomic exchange interaction

The analysis of the CTC-Kβ is of particular interest for magnetic semiconductors because it permits probing (indirectly) the local magnetic moment brought by the 3d TMs impurities without the need for a demanding sample environment such as low temperature and high magnetic field. In fact, CTC-Kβ is sensitive to the net local 3d spin moment, independently of its direction. This gives the possibility of studying a magnetic material even in the paramagnetic state, that is, when the local moments are fluctuating and pointing in random directions. As shown in figure 8 for three Mn-oxide powder samples (MnO, Mn2O3, MnO2), the Kβ main lines evolve with the decreasing nominal spin state (S, SmnO = 2.5 \rightarrow SmnO₂ = 2): the Kβ′ shifts toward lower energy and the Kβ″ reduces in intensity; this means that the center of mass energy (the sum of the energies of all final states weighed by their intensities) does not change between the configurations but the Kβ′′-Kβ″ splitting decreases with decreasing spin state. This behavior is understood in a total energy diagram (inset of figure 8). The intra-atomic exchange energy between the 3p hole and the 3d levels (sum of the Slater exchange integrals, J) lowers the total energy. As a consequence, the configurations with parallel spins are lower in energy than the configurations with paired spins.

The Kβ transition involves core levels and multiplet ligand-field theory is therefore the appropriate framework to discuss the spectral features [142–144]. In order to better understand the spin-polarized origin of the Kβ emission for a 3d TM, we take as example the 3d⁵ configuration, an atomic
picture and a two-step process [145] (as shown in figure 9(a)). A 3d\(^3\) high spin configuration is a favorable case because of the absence of an orbital angular momentum in the ground state. Hund’s rule dictates that all spins are aligned, giving the \( ^6S \) ground state spin–orbit term. Photoionization then excites the system to the \( 1s3d^2\pi e_p \ ( ^5S \) intermediate states. The \( ^7S \) term can only decay into the \( ^3P \), while the \( ^5S \) one decays into all interacting \( ^3P \) states (where symmetry mixing is important). In consequence, the K\(\beta'\) originates almost 100\% from spin-down transitions and the K\(\beta_{1,3}\) primarily from spin-down. This result is exemplified in figure 9(b) via a one-electron picture of the final state. The strong spin selectivity was demonstrated to be valid also when the atom is inserted in a crystal field [144]. In fact, neglecting orbital mixing, the K\(\beta\) lines do not depend on the fine structure in the valence shell (e.g. crystal field splitting) as long as the spin state does not change. On the other hand, a strong crystal field splitting may result in a spin–orbit term mixing and thus the shape of K\(\beta\) lines varies. In conclusion, the spin selectivity is conserved and it is employed to record spin-selective XAS (see section 7.1), while the spectral features change and the methods to take them into account are discussed in the following.

To perform a quantitative analysis of the CTC-K\(\beta\), the first method is to approximate the energy separation and the intensity ratio between K\(\beta_{1,3}\) and K\(\beta'\) by \( \Delta E = J(2S + 1) \) and \( I/\langle I\rangle = S/(S + 1) \) [147]. This approximation is found to reproduce fairly well the experimental results if a peak fitting procedure is employed [148–150]. On the other hand, a peak fitting procedure is prone to errors in the extraction of the peaks positions and arbitrary in the choice of the number and form of the fitted functions. To overcome the problem of linking the data analysis to a theoretical approximation, fully experimental data reduction methods were put in place. The first attempt was to use the first moment energy of the K\(\beta_{1,3}\) [145, 151] \( \langle E \rangle = \sum_j \langle E_j I_j \rangle / \sum_j I_j \). Recently, another and more accurate procedure was proposed [152, 153]. It is based on the integrated absolute difference (IAD) of spectra

\[
IAD_\beta = \int \frac{\sigma_X^\text{ESE}(E) - \sigma_0^\text{ESE}(E)}{\sigma_0^\text{ESE}(E)} \, dE
\]  

where the XES spectrum \( \sigma_0 \) is taken as reference \( (IAD_\beta = 0) \) and \( \sigma_X \) is the spectrum for which the IAD value is determined. Often the IAD values are determined versus a given parameter within a series (e.g. pressure, temperature, concentration, doping) but the method can be applied to any spectra. It is based on the differences in the whole spectral range and results in a more robust procedure, especially when dealing with weak moments. It was successfully applied to determine the evolution of the local magnetic moment.
Figure 9. Kβ emission process after photoionization illustrated for a 3d^5 case. Left panel (a): atomic multiplet theory. Right panel (b): simplified one-electron picture (not in energy scale) where paired electrons and the spin flipping in Kβ_{1,3} are omitted for clarity. A detailed description is given in the text.

Figure 10. IAD analysis for a series of Mn-oxides with respect to MnO. The inset shows how the IAD is obtained for Mn_2O_3. (S) in iron-based superconductors [154–156] or in strongly correlated oxides [157–159]. To illustrate the method in practice, the IAD analysis for a series of polycrystalline Mn-oxides (commercially available powders) is shown in figure 10. The IAD values of the normalized spectra are obtained using MnO as reference (IADMnO = 0) and are related to the nominal spin state, assuming an ionic approximation and a high-spin scenario. Subsequently, a linear fit permits obtaining a relative calibration that accounts for all possible effects: changes in oxidation state, bond lengths and angles, site symmetry, energy shifts during the experiment. By taking into account all these effects, the error bar on the IAD values is comparable with the size of the symbols of figure 10. This makes such analysis very accurate and reproducible. Once the IAD values are calibrated on model compounds, it is possible to follow the evolution on real samples. For DMS/CMS one usually wants to follow the evolution versus the magnetic dopant concentration or the ratio with shallow impurities in the case of co-doping.

To overcome the crude ionic approximation and to take into account the covalent bonds in a material (charge transfer), better results are obtained if the IAD values are compared or calibrated to an effective local spin moment, S_{eff}, defined as

\[ S_{eff} = \frac{1}{2} (\rho_{A,j}^+ - \rho_{A,j}^-) \] (8)

where \( \rho_{A,j}^{\pm} \) is the calculated spin density (charge) on the atom A and projected on the orbital angular momentum \( l \). The projection over \( l \) permits having an effective quantity comparable to the spectroscopic measurement. In fact, although the charge of an atom in a crystal or molecule is not a good quantum mechanical observable [161, 162], the inner-shell spectroscopist is tempted to assign atomic properties. Many quantum chemical approaches exist [163], but in DFT the standard methods to perform a population analysis are those introduced by Mulliken [164], Löwdin [165] and Bader [166]. In the Mulliken or Löwdin analysis the charges are equally divided between two atoms of a bond; this has the advantage of simplicity. A different approach is followed for the Bader populations: the electron densities are integrated in a volume defined by the gradient of the electronic density function. This scheme usually gives the best results.

The combination of the IAD analysis with S_{eff} calculated \textit{ab initio} using DFT has been recently applied in the study of Mn–Mg substitutional complexes in Ga_{1−x−y}MnxMgyN [167]. As shown in figure 11, the IAD are employed to follow the evolution of the Mn spin state as a function of the ratio between the Mg and Mn concentration in GaN. By calibrating the IAD values to the Mn-oxides reference compounds using an ionic approximation, it is possible to extract a nominal spin state. This is then compared to S_{eff} calculated via DFT. Both evolve in the same way and differ only by a rigid shift (≈0.2 in this case). This shift originates from the ionic approximation used to calibrate the IADs. In fact, the correct procedure to extract a better absolute measurement of \( S \) is to calibrate the IAD via the Bader analysis performed also on the model compounds. By doing so, one finds S_{MnO} = 2.2, in perfect agreement with S_{eff} calculated for Mg/Mn = 0 in figure 11. This confirms that the IAD analysis with an \textit{ab initio} S_{eff} is accurate in following the evolution of the local spin moment.
As described for VTC-K$_{\beta}$, also in CTC-K$_{\beta}$ it is possible to make use of the polarization dependence. For example, Herrero–Martin et al [159] studied the spin distribution in La$_{1-x}$Sr$_x$MnO$_4$. They found that increasing the number of holes (i.e., increasing $x$) changes the total charge (and spin) on Mn very little, but the tetragonal distortion, that is greatly reduced when going from $x = 0$ to $x = 0.5$, causes an anisotropic spin distribution that also disappears upon hole doping.

7.1. Spin-selective XAS

Spin-selective XAS was first exploited by Hämmiläinen and co-workers [168] and then described via LFMT [143, 169]. This technique is based on the strong spin polarization of CTC-K$_{\beta}$ emission lines (as previously described in section 7): by collecting a HERFD-XAS spectrum tuning the spectrometer to the K$\beta_{1,3}$ and K$\beta'$, it is possible to select, respectively, the transitions to the spin down and spin up density of states (in a one-electron picture). We underline that the spin-selectivity in this technique arises only from the K$\beta$ spectrum, that is, the spin has a local internal reference that does not change in energy for a change in the direction of the spin moment. With respect to XMCD, circularly polarized light and an external magnetic field (external reference) are not required. The link between the two techniques resides in the energy dependence of the Fano factor [170].

An example of application of this technique to the characterization of magnetic semiconductors was reported recently [171]. The Mn K-edge HERFD-XAS spectra of ZnO/Zn$_{1-x}$Mn$_x$O core/shell nano-wires were measured at K$\beta_{1,3}$ and K$\beta'$, then compared to ab initio DFT calculations using a FLAPW approximation. As shown in figure 12, the spectral features A, B$_{1,2}$, C$_{1,2,3}$ and D are reproduced by the theory (panel a), in agreement between the two spin-polarizations. This agreement was obtained using a Mn defect substitutional of Zn (MnZn) in a ZnO relaxed supercell. Of particular interest for DMSs is the pre-edge region where the electronic structure of the spin-polarized MnZn impurity level can be studied in detail. In the case of zincblende and wurtzite DMSs, the local symmetry around the cation is tetrahedral (T$_D$) in first approximation (we do not take into account the Jahn–Teller effect [172]), this means that the TM $d$ states are split by the crystal field into $e$ (doublet) and $t_2$ (triplet) levels. As reported in the panel b of figure 12, they are fully spin polarized. In addition, because of the $t_2$ symmetry, they can partially couple with the $p$ bands [35]. Electric dipole transitions to $t_2$ dominate over quadrupole ones to $e$ [173], this explains why the spin-selective XAS technique is extremely sensitive in the pre-edge region to the fine details of the electronic structure of these materials.

8. RIXS and magnetic circular dichroism

RIXS can be coupled with magnetic circular dichroism (RIXS-MCD) using circularly polarized x-rays and an external magnetic field applied to the sample. In selected cases, RIXS-MCD permits to combine the benefits of hard and soft x-rays XMCD by selecting specific final states. The idea is to make use of hard x-rays and reach a spin-orbit split final state indirectly via an intermediate state (see total energy diagram in figure 2), where the dichroism arises from the coupling of the magnetic moment of the absorbing atom with the circularly
polarized light. The first application of RIXS-MCD was at the L_{2,3} pre-edges of RE elements, where the quadrupole transition channel [175] (2p → 4f), was used to probe with hard x-rays and via a second-order process the same final states obtained with direct dipole transitions in M_{4,5} lines XMCD [176–180]. Recently, this approach was successfully applied also to the K pre-edges of TM elements [174], extending the possibilities of K-edge XMCD. For TMs, the required intermediate state can be excited either via quadrupole transitions (1s → 3d) or dipole to mixed 3d-4p states. This means that RIXS-MCD cannot be applied to metals, but to TMs-doped semiconductors and insulators or bulk TMs oxides and nitrides.

In figure 13 we show the application of RIXS-MCD to magnetite (Fe_{3}O_{4}) as reported in [174]. Magnetite is a ferrimagnetic inverse spinel with a Curie temperature of 860 K, high spin polarization at room temperature, good magnetostriction and showing a metal–insulator transition at about 120 K [181] (Verwey transition). These properties make the material very appealing for spintronics heterostructures. It is a challenging material also from the characterization point of view (see [182, 183] plus references therein). It is commonly accepted that Fe_{3}O_{4} has two differently coordinated and antiferromagnetically coupled sublattices (T_{D} and O_{h}), with mixed valences on the O_{h} site (Fe^{2+} and Fe^{3+}) and with Fe^{3+} mainly responsible for the resulting magnetic moment. In synthesis, its formula can be written as Fe^{3+}_{T_{D}}Fe^{2+}_{O_{h}}O_{4}. The total absorption (figure 13(a)) shows the pre-edge region resolved in the Kα_{1,2} spin-orbit split emission lines, that is, 1s2p RIXS. The detailed structure of the Fe pre-edge features was extensively described for XAS [35] and RIXS [184]. We can summarize, in a nutshell, that the features arising at ≈7114 eV incident energy and ≈710 eV energy transfer are from Fe^{3+}, while those at ≈7112 and ≈707 eV from Fe^{2+}. This shows as a broadening in the diagonal direction in the RIXS plane. The effect is more visible on the Kα_{1} line (due to a better signal-to-noise ratio).

In figure 13(b) the circular dichroism (right minus left circular polarization) is shown for the experiment and the
theory. The simulated 1s2p RIXS-MCD plane is based on ligand-field multiplet calculations for Fe$_3^{3+}$ only. As demonstrated in [174], the strong dichroism originates in part from the sharpening effect (as described in section 5) but mainly from the 3d spin–orbit interaction in the intermediate state and the 2p–3d Coulomb repulsion combined with the 2p spin–orbit interaction in the final state. The main spectral features are reproduced by the calculation, confirming that the Fe$_3^{3+}$ site is dominating the measured signal. By taking a vertical cut along the energy transfer (figure 13(c), top), the resulting line scan is comparable with a L$_2$-L$_3$ XMCD spectrum, both in the sign—plus/minus (minus/plus) for Ko$_1$ (Ko$_2$)—and the amplitude. The enhancement in amplitude with respect to a conventional K-edge XMCD is one of the advantages of RIXS-MCD. In addition, the RIXS-MCD plane shows an extra feature in the region ascribed to Fe$_2^{3+}$ (see figure 13(b)). This feature is not reproduced when only Fe$_3^{3+}$ site is taken into account and its weak intensity permits interpreting it as originating from Fe$_2^{3+}$ mainly [174]. A diagonal cut at the Ko$_1$ maximum also shows it (figure 13(c), bottom).

This demonstrates that it is possible to use RIXS-MCD both as element- and valence-/site-selective magnetometer by means of field dependent measurements [185]. In magnetic semiconductors, this technique would permit disentangling the extrinsic magnetism coming from metallic precipitates from the intrinsic one.

9. Conclusions and future developments

In this review we have presented the basic elements of x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS) spectroscopies, with a focus on the characterization of magnetic semiconductors and employing hard x-rays. The theoretical background (Kramers–Heisenberg equation), the required experimental setup and the approaches to the calculations are the building blocks for a practical introduction to the field. With respect to doped semiconductors, XES and RIXS play a crucial role in studying the local electronic structure around the Fermi level. By using the VTC-$K\beta$ it is possible to directly probe the ligand states in the valence band, while the CTC-$K\beta$ is a sensitive tool of the local spin angular momentum, via intra-atomic exchange interaction. We have also shown that with RIXS (or spin-selective XAS) it is then possible to complement the electronic structure picture by probing unoccupied states (conduction band) with spin sensitivity. Finally, RIXS-MCD permits extending the element-selective magnetometry (x-ray magnetic circular dichroism) by gaining in signal intensity plus in site- and valence-selectivity.

Supported by the fast evolution in the theoretical tools and the development of new instrumentation, the users community in this field is growing. This gained momentum permits not only better analysis of current data, but also prediction and realization of new challenging experiments. In particular, the materials scientist working with strongly correlated materials will benefit from a photon-in/photon-out spectroscopy in the hard x-ray spectrum. In fact, this technique will permit characterizing, at the atomic level, devices in operating conditions (e.g. a spin field-effect transistor with applied gate voltage), with the possibility to perform direct tomography [186]. Magneto-optical devices can be characterized in a laser pump and x-ray probe configuration to study fast spin dynamics as spin–orbit interaction [187] or spin state transitions [188].

RIXS experiments require the high brilliance of third generation synchrotron radiation sources or even x-ray free electron lasers, that is, high photon flux with small divergence and small energy bandwidth. However, XES is a powerful tool which can be accessible also outside large-scale facilities. In fact, the advantage of XES is that it can be performed with a pink beam. This permits adapting an XES instrument on any synchrotron radiation beamline (e.g. standard XAS, x-ray diffraction, imaging) or on a laboratory x-ray tube. For example, one can take the case of measuring Mn CTC-K$\beta$ on a Ga$_0.97$Mn$_{0.03}$N thin film (dilute material in a strong absorbing matrix). By a simple comparison only on the incoming photon flux, assuming $10^9$ ph s$^{-1}$ (e.g. from a rotating anode x-ray tube) one would get $\approx$10 counts s$^{-1}$ on the Mn CTC-$K\beta$ maximum. Considering the very low background of a point-to-point spectrometer, a spectrum with a reasonable signal-to-noise ratio is obtained in one day of measurements.

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