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Applications of soft x-ray magnetic dichroism

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Abstract. Applications of x-ray magnetic circular and linear dichroism (XMCD and XMLD) are reviewed in the soft x-ray region, covering the photon energy range 0.4-2 keV, which includes important absorption edges such as the 3d transition metal \(L_{2,3}\) and rare earth \(M_{4,5}\). These techniques enable a broad range of novel and exciting studies such as on the electronic properties and magnetic ordering of novel nanostructured systems. XMCD has a sensitivity better than 0.01 monolayer (at the surface) and due to simple detection methods, such as electron yield and fluorescence yield, it has become a workhorse technique in physics and materials science. It is the only element-specific technique able to distinguish between the spin and orbital parts of the magnetic moments. The applications are vast, e.g., in x-ray holographic imaging, XMCD gives a spatial resolution of tens of nm. While many studies in the past were centered on physics, more recently new applications have emerged in areas such as chemistry, biology and earth and environmental sciences. For instance, XMCD allows the determination of the cation occupations in spinels and other ternary oxides. In scanning transmission x-ray microscopy (STXM), XMCD enables us to map biogenic magnetite redox changes resulting in a surprising degree of variation on the nanoscale. Another recent development is ferromagnetic resonance (FMR) detected by time-resolved XMCD which opens the door to element-, site- and layer-specific dynamical measurements. By exploiting the time structure of the pulsed synchrotron radiation from the storage ring the relative phase of precession in the individual magnetic layers of a multilayer stack can be determined.

1. Introduction
The effect of magnetic x-ray dichroism was discovered in the Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE) at Université Paris-Sud in France in 1986 [1], only one year after its prediction [2]. A sum rule, derived in 1992, relates the integrated intensity of the x-ray magnetic circular dichroism (XMCD) spectrum over the x-ray absorption edge to the ground-state orbital magnetic moment [3]. This has transformed XMCD into a powerful standard technique to determine spin and orbital magnetic moments, providing insight in the element-specific microscopic origin of anisotropic magnetic properties, such as the magnetocrystalline effect, easy direction of magnetization, magnetostriction, coercivity and magnetic hysteresis. X-ray magnetic linear dichroism (XMLD) makes it possible to measure antiferromagnets, which have no net total magnetic moment.

The soft x-ray region covers the important edges for transitions from core levels into empty magnetic states: the 3d transition metal \(L_{2,3}\) (\(2p \rightarrow 3d\), at 0.5-1 keV), rare earth \(M_{4,5}\) (\(3d \rightarrow 4f\), at 0.8-1.6 keV) and actinide \(N_{4,5}\) (\(4d \rightarrow 5f\), at 0.7-1.5 keV). Soft x-ray excitations have considerable advantages over hard x-rays. They give huge resonances corresponding to dipole-allowed transitions directly into the magnetic valence state. Polarization dependent selection
rules result in a multiplet structure that serves as a fingerprint for the ground state electronic and magnetic structure.

The XMCD is defined as the difference between the x-ray absorption spectra (XAS) for antiparallel and parallel configuration of the light helicity and magnetic field direction. In a simple picture, the XMCD process can be visualized as a two-step model. The 2p core level is split in a \( j = 3/2 \) state (\( L_3 \) edge) and \( j = 1/2 \) state (\( L_2 \) edge), where spin and orbit are coupled parallel and antiparallel, respectively. In the first step, the emission with the light helicity vector parallel (antiparallel) to the 2p orbital moment results in excited electrons of preferred spin up (down) direction. In the second step these excited electrons have to find a place in the 3d valence band, and if there are less spin-up than spin-down holes available, the XMCD spectrum displays net negative \( L_3 \) and positive \( L_2 \) peaks [cf. Fig. 1(b)].

Interesting applications arise when the XMCD or XMLD effect is used in magnetic x-ray holography, x-ray detected ferromagnetic resonance (XFMR) or x-ray photoemission electron microscopy (PEEM). Magnetic dichroism in magnetic x-ray resonant scattering enables the investigation of (anti)ferromagnetic lattices, magnetic roughness versus chemical roughness, relative spin orientations, non-collinear moments and magnetic domain structures [4, 5, 6].

2. Advantages of soft x-ray spectroscopy

It is useful to emphasize the main advantages of soft x-ray spectroscopy [7].

(i) **Element-specificity.** Sensitivity to a chemical element is obtained by tuning the x-rays to the resonance energy of the core to valence transition. When various layers contain different elements, this turns into a layer specific probe.

(ii) **Orbital sensitivity.** The light interacts only with the orbital part of the wave function, so that spin and orbital properties can be separated. This allows to study specific orbital effects, such as orbital ordering and Jahn-Teller effect.

(iii) **Selection rules.** Electric-dipole transitions from the ground state can reach only a limited subset of final states, thereby providing a fingerprint for the specific ground state. This gives a high sensitivity to crystal field, spin-orbit interaction, site symmetry and spin configuration [8].

(iv) **Magnetic sensitivity.** The light polarization dependence makes the absorption sensitive to the ground state magnetic polarization. The magnetic dichroism is strong because it arises from the electric-dipole and not the magnetic-dipole transitions [8].

(v) **High energy resolution.** The core hole life time broadening is of similar magnitude as the instrumental resolution. This narrow intrinsic broadening, in the order of a few hundred meV, makes it possible to resolve the detailed multiplet structure and charge-transfer satellites.

(vi) **Well-defined core-level states.** X-ray transitions involving a core state are much more straightforward to calculate than optical transitions. The wave function of the core state is well defined and mixing (hybridization) between core and valence states can be neglected. In localized materials the presence of spin-orbit and electrostatic interactions leads to a unique multiplet structure. The core-level state is therefore an ideal probe to study the local electronic configuration of the valence states.

(vii) **Fundamental spectra.** The angular dependent part of the spectra can be separated from the physical (dynamical) part. This provides the powerful concept of fundamental spectra [9, 10, 11].

(viii) **Sum rules.** Summation over a core-level state with a good quantum number (such as total angular momentum, \( j \)) fulfils the completeness relation. This provides the theoretical basis of the sum rules.

(ix) **Femtosecond time scale.** In localized systems, the x-ray transition is much faster than the rearrangement of the valence electrons. This means that calculations can be done in the limit of the sudden approximation. Compared to Mössbauer spectroscopy, XAS is much faster, perceiving in magnetite the Fe\(^{2+}\) and Fe\(^{3+}\) cations on the octahedral sites as ‘frozen’ [12, 13].
itinerant systems such as metals, the femtosecond time scale of the core-hole clock can be used to monitor the electronic screening processes [14, 15].

3. X-ray absorption—the basics

3.1. The magneto-optical effect

It is illustrative to compare the XMCD effect with the magneto-optical Faraday or Kerr effect. The optical spectra are due to excitations from occupied valence band to unoccupied conduction band states, as schematically shown in Fig. 1(a). Selection rules ($\Delta m = -1$ and +1) for the orbital component result in a different transition probability for left- and right-circularly polarized light into the unoccupied polarized valence band. Since the light does not interact directly with the spin, but only indirectly via the spin-orbit interaction, the dichroism increases in first instance with the spin-orbit interaction, which in the optical region is relatively weak ($\sim$50-100 meV for 3d atoms). However, a very strong dichroism is obtained in the case of XMCD, since the core-level spin-orbit interaction is much larger (tens of eV), resulting in pure $j = \ell \pm s$ levels, as depicted in Fig. 1(b).

Magnetic dichroism in photoemission can be described similarly as in x-ray absorption, but there are some differences. In absorption the dichroism is a consequence of the Pauli principle. The polarized light creates polarized electrons which can not go freely into the magnetic 3d shell. In contrast, in x-ray photoemission spectroscopy (XPS) the core electron is ejected into a continuum shell which has no interaction, and the dichroism arises from the electrostatic interaction between the core hole and the polarized 3d electrons [9]. Magnetic dichroism furthermore plays an important role in second-order coherent processes, such as resonant diffraction, resonant inelastic x-ray scattering (RIXS), resonant photoemission (RESPES), etc., as has been described elsewhere [16].

3.2. Calculational aspects

For localized many-electron systems, transitions are of the type $d^n \rightarrow p^5 d^{n+1}$ (or $f^n \rightarrow d^9 f^{n+1}$ in case of rare earths and actinides). The polarized XAS spectra can be calculated using multiplet theory [17], which puts the spin-orbit and electrostatic interaction on an equal footing [18]. The electrostatic interaction includes the $p-d$ and $d-d$ Coulomb and exchange interactions. The wave functions of the initial- and final-state configurations are calculated in intermediate coupling using Cowan’s atomic Hartree-Fock (HF) code with relativistic correction [19, 20, 8, 17]. The HF values of the Slater parameters are normally reduced to 70-80% to account for configuration interaction and screening effects. Such a reduction was found to give the optimal scaling for the rare-earth $M_{4,5}$ XAS [21, 17]. The spin-orbit parameters are usually kept within a few percent of their atomic values.

Crystal- and ligand-field interactions are taken into account using Butler’s chain of groups method [22, 23]. Hybridization (mixing) can also be taken into account, resulting in charge-transfer satellites [24]. The calculations show that the spectral shape of XAS, XMCD and XMLD is strongly sensitive to the character of the 3d$^n$ ground state [8, 25].

At finite temperatures a Boltzmann distribution is taken over the energy levels of the initial state [2]. This is especially important when the ground-state degeneracy is lifted by the 3d spin-orbit interaction, giving rise to a bunch of low energy levels, such as in the case of CoO [26].

3.3. Sum rules

Sum rules provide a theory-independent method to obtain ground-state properties. They are valid for localized as well as itinerant electron systems, and in fact theory independent. Sum rules for the isotropic XAS relate the total integrated intensity to the number of valence holes, $n_h$ and relate the core-level spin-orbit split branching ratio to the angular part of the spin-orbit interaction.
Figure 1. (a) Magneto-optical Faraday and Kerr effect. (b) XAS/XMCD effect in core-level spectroscopy. (c) Relative contributions to the energy dependence of the Fe 2p XMCD spectrum arising from the different ground state moments for iron metal. $n_h$ = number of holes, $\ell \cdot s$ = scalar part of spin-orbit interaction, $L_z$ = orbital moment, $S_z$ = spin moment and $T_z$ = magnetic dipole term. The red and blue spectra relate to the sum rules for the orbital and spin magnetic moments, respectively. The upper spectrum shows the sum of all contributions, which resembles the experimental Fe $L_2,3$ XMCD spectrum. For further details see Ref. [27].
dichroism is related to the charge quadrupole moment. The light does not interact directly with the electron spin, but spin dependent operators can be obtained when the integrated intensities are weighted appropriately over the two spin-orbit split core levels. Using these weighted integrals the ground state spin-orbit coupling is obtained from the isotropic spectrum; the spin moment and magnetic dipole term are obtained from the circular dichroism; and the spin-orbit-induced quadrupole moment is obtained from the linear dichroism [38].

3.4. Ground state moment contributions

We will now illustrate the sum rules from the perspective of the different ground-state moments. In Fig. 1(c) the Fe L2,3 XMCD spectrum is decomposed into its contributions from the separate ground-state moments [27, 39]. It can be seen that only for the orbital moment, Lz, the XMCD has a non-zero intensity integrated over both edges. For the spin moment, Sz, and magnetic dipole term, Tz, the XMCD does not vanish over each separate edge but integrated over both edges the intensity is zero. For the number of valence holes, nh, and the spin-orbit interaction, ℓ · s, the integrated intensity of of XMCD vanishes for each edge, but they still give an energy dependence across each edge. This is also the case for the higher moments, such as the quadrupole moments, as demonstrated elsewhere [27]. Hence, this not only illustrates that the integrated intensities over the L3 and L2 edges are proportional to the orbital and spin moments, but also that they do not depend on any of the other ground state moments. Since all moments contribute to the energy dependence, the sum rules in their differential formulation [40] are not exact.

3.5. Influence of the 3d spin polarization

The main contributions in the XMCD normally come from Sz and nh, with the other ground-state moments usually much smaller. From Fig. 1(c) it is clear that nh gives a strong energy dependence across each absorption edge. To simplify the analysis, we will condense Sz and nh into a single parameter, i.e., the spin polarization PS which is the difference between the amount of spin-up, n↑, and spin-down, n↓, holes (where n↑ ≥ n↓), divided by the total amount of holes,

\[ PS \equiv \frac{n^\uparrow - n^\downarrow}{n^\uparrow + n^\downarrow} = \frac{S_z}{n_h}. \] (1)

Fig. 2(a) shows the XMCD with the spin polarization PS stepwise varying from 0 (where n↑ = n↓) to 1 (where n↓ = 0). The L3 line shape of the XMCD changes from very symmetric for PS = 1 to very asymmetric for PS = 0 [39]. This trend of increasing asymmetry is confirmed experimentally as seen in Fig. 2(b), which shows the XMCD of the pure metals along the 3d transition-metal series [41], in which PS reduces going from Ni towards V metal. Note that the experimental spectra for Ni and V metal also reveal some peculiarities. Nickel metal shows a pronounced satellite structure due to correlation effects in the ground state [24]. The spectrum of vanadium metal has a complicated structure with overlap between the L3 and L2 features [42].

The peak asymmetry of the L3 XMCD is inversely proportional to the spin polarization [39]. The positive lobe at the high energy side of the L3 in the XMCD can be taken as a measure for an unoccupied spin-down band. It is absent in hard ferromagnets where the spin-down band is full and the holes are in the spin-up band. The experimental spectra in Fig. 2(b) show indeed that the positive lobe is absent in Ni and Co metal and starts to appear in Fe metal, in good agreement with the calculated majority and minority 3d spin density of states [43]. XMCD measurements from galfenol (GaₓFe1−ₓ alloy) thin films reveal a gradual change in magnitude of the positive lobe as a function of composition, which can be related to a change in the electronic structure of this material that exhibits extraordinary magnetoostrictive properties.
Figure 2. (a) Calculated 3d metal \( L_{2,3} \) XMCD for varying 3d spin polarization \( P_S = -S_z/n_h \), with \( \ell \cdot s \), \( L_z \), \( T_z \) and 2p spin-orbit splitting kept at constant values [39]. (b) Experimental \( L_{2,3} \) XMCD spectra of the 3d transition metals [41]. The 2p spin-orbit splitting gradually reduces for lighter elements, as shown by the dotted lines.

[44]. In magnetostrictive thin films the adaption to new dimensions is inhibited by bonding to the substrate; and applying a magnetic field in the film plane does not result in an expansion or contraction along the field direction. Instead a magnetoelastic stress is created that leads to a change in the magnetocrystalline anisotropy.

4. Detection and surface sensitivity
In the soft x-ray region the absorption at resonance is very strong and proportional to the number of 3d or 4f holes. Henke’s data tables [45], which are valid for off-resonance excitation, provide no assistance here. For instance, the x-ray attenuation length for pure Fe just below the \( L_3 \) edge is 591 nm, but at the maximum of the \( L_3 \) and \( L_2 \) edge it is 16.7 and 32 nm, respectively [28]. At the rare earth \( M_5 \) edge the x-ray attenuation length is even shorter, i.e., 6.2 nm for Gd and and 12.1 nm for Dy. It was at the rare earth \( M_{4,5} \) edges that saturation effects in total electron yield (TEY) detection were first quantified [21, 46].

TEY is by far the most practiced detection method in the soft x-ray region. It gives a high surface sensitivity with a sampling depths of \( \sim 3 \) nm [47, 48]. As long as the sampling depth remains much shorter than the x-ray attenuation length, the TEY signal represents the true (photon energy dependent) absorption coefficient very well. Due to its high surface sensitivity, TEY is ideal for monolayer coverages and magnetic adatoms, capable of measuring the XMCD of 0.005 of a monolayer coverage [49].

In transmission measurements, samples have to be very thin because of the strong absorption. Samples can be produced as thin films and multilayers, although one should take care to avoid
saturation effects [50]. Thin films grown on MgO or sapphire can be measured using the luminescence from the substrate, which is excited by the transmitted x-rays not absorbed in the sample.

Fluorescence yield (FY) probes deeper than TEY, but the signal is low in the soft x-ray region. Also the spectrum obtained by FY can have a different shape as the x-ray absorption, due to the specific excitation de-excitation process [51]. This is no real problem for measurements done at fixed photon energy, such as in the case of XMCD hysteresis loops [52] and XFMR [53].

5. Spintronics applications

5.1. Device development

Introduction of controlled thin film deposition and lithographic patterning methods has brought about a renaissance in magnetism research. The possibility to engineer multilayers of magnetic and non-magnetic metals on the nanoscale led to the discovery in the late eighties of interlayer exchange coupling and giant magnetoresistance (GMR). Confining the dimensions of a magnetic structure to the magnetic exchange length scale or the domain wall length results in intriguing phenomena, unknown to bulk materials. Apart from their scientific interest, the technological potential of GMR devices and nanostructured materials is an important driving force for the study of magnetic thin films and nanostructures. GMR magnetic field sensors were introduced within 10 years of the discovery of the GMR effect and are nowadays indispensable for automotive applications and data storage. Tunnel magneto-resistant junctions form the core of non-volatile magnetic random access memories (MRAM).

Many methods are used to characterize the magnetism of thin films and confined magnetic structures. Among these, magneto-optical methods offer the advantage not to be hampered by magnetic and electric fields. However, magneto-optics in the visible range is not element-specific and moreover the spatial resolution is limited by the wavelength. Element-specific XMCD on magnetic elements has opened up new possibilities [1, 2, 54], which strongly benefit from the advent of undulator devices with variable linear and circular polarization.

Organic magnetic materials possess a number of chemical properties that may provide new processing strategies and new applications, such as electro-optic and opto-magnetic materials.

Scattering experiments are mostly performed using hard x-rays, which offer high spatial resolution and large penetration, hence a narrow Darwin width of the Bragg peaks. However, in the soft x-ray range the resonant magnetic scattering cross-sections are orders of magnitude larger, and if the soft x-ray wavelengths are not too large for determination of the unit cell structure, they are ideally suited to resolve the micromagnetic structure of domains and artificially structured devices [5, 55].

5.2. Time resolved spectroscopy and imaging

Knowledge of the time domain structure is critically important due to the need for increased read-write speed of magnetic information. Interesting magnetic phenomena are displayed in a wide range of exploratory materials, such as biomagnets, molecular magnets, oxide magnets and soft magnets. Fundamental questions exist about the nature of domain wall motion and precessional reorientation in confined magnetic structures [56].

Time resolved x-ray measurements complement optical pump-probe studies that aim to determine the most effective means of reversing the magnetization of a thin film or nanostructure in the shortest possible time. So far the role of interfaces and edges upon the reversal process is poorly understood. The local nature of time-resolved XMCD measurements may provide new insight into this problem, which is of vital importance to the future of the data storage industry.

The pulsed nature of synchrotron radiation provides an inherent capability for stroboscopic measurements of picosecond magnetic processes. The timing pulse generated by the synchrotron can be used to trigger a pulsed magnetic field in a stripline or micro-coil structure. Time resolved
XMCD has been used to resolve the nanosecond dynamics of individual layers within spin and tunnel valve structures [57], while time resolved spin polarized photoemission was used to isolate the signal from the surface region [58]. Time resolved magnetic images with spatial resolution of down to 20 nm were obtained with x-ray photoelectron emission microscopy (XPEEM) [59, 60]. Other synchrotron-based studies include full-field magnetic transmission microscope images of magnetization dynamics.

Increased data rates are required in magnetic recording technology in order to exploit recent gains in areal density and storage capacity. High-speed magnetic reorientation is a generic problem underlying the operation of all parts of hard disk systems, MRAM, and to some extent magneto-optical recording. The existing technology is at a watershed where thermal activation and domain wall motion are being supplanted by precessional mechanisms. Different material properties, for example anisotropy and damping, are required in these high frequency applications, and it is necessary to characterize the materials at the frequencies at which they are used.

5.3. Diluted magnetic semiconductors

Diluted magnetic semiconductors are expected to play an important role in interdisciplinary materials science and future spintronics because the integration of charge and spin degrees of freedom will deliver new types of devices for information storage and processing. Magnetic semiconducting materials such as EuO have been known for many decades, but have remained a scientific curiosity due to the fact that the ferromagnetic phase was always only found at low temperatures requiring helium cryogenics.

In the past decade or so, the concept of a diluted magnetic semiconductor, where a magnetic species is doped into a conventional semiconducting material has received large attention, as it potentially offers the promise of room temperature ferromagnetism in a semiconducting material [61]. Probably the best studied system to date is Mn$_x$Ga$_{1-x}$As, which is widely accepted as a truly ferromagnetic material, with a Curie temperature below room temperature [62]. Fig. 3(a) shows the ferromagnetic coupling between two Mn atoms in the zinc blende crystal structure of GaAs. The experimental Mn $L_{2,3}$ XMCD of (Ga$_{0.93}$Mn$_{0.07}$)As thin film is reproduced in Fig. 3(b) and agrees very well with multiplet calculations [63]. The orbital and spin magnetic moments are 0.15 $\mu_B$ and 4.3 $\mu_B$, respectively, as derived from the sum rules for the integrated $L_{2,3}$ intensities.

A large number of other systems has been investigated both theoretically and experimentally, with GaN and the semiconducting metal oxides such as ZnO, TiO$_2$ and SnO$_2$ receiving large interest due to the theoretical results predicting room temperature ferromagnetism for the correct level of dopant Mn, Fe or Co atoms [61]. Experimental results so far are mixed, as all these materials rely on levels of magnetic species far above the solubility limit, so that non-equilibrium growth techniques are needed to prepare them successfully. Failure will result in phase segregation leading to clusters of the magnetic atoms, which will exhibit a ferromagnetic signal to bulk probes such as conventional magnetometers. XMCD is precisely the technique whereby such cluster dominated systems and secondary phases can be distinguished from those that are truly dilute [64].

6. Environmental sciences

6.1. Cation occupancies

In nature, spinel ferrites are common constituents of igneous rocks, often in concentrations of economic importance and are the main contributors to rock magnetism [65]. Complex chemistries and cationic distributions result in a range of electric and magnetic properties that have motivated extensive mineralogical and technological investigations.
Figure 3. (a) Zinc blende crystal structure of GaAs with ferromagnetic coupling between two substitutional Mn atoms on Ga sites (Ga = blue spheres, Mn = green spheres and As = black spheres). (b) Experimental Mn $L_{2,3}$ XAS for positive (black line) and negative (red line) applied magnetic field and resulting XMCD (green line) of 50 nm (Ga$_{0.93}$Mn$_{0.07}$)As film [63].

Magnetite has a cubic spinel crystal structure with a unit cell containing 32 oxygen ions, eight Fe$^{3+}$ ions at tetrahedral ( ) sites, eight Fe$^{2+}$ and eight Fe$^{3+}$ ions at octahedral ( ] ) sites, i.e., (Fe$^{3+}$)[Fe$^{2+}$Fe$^{3+}$]O$_4$. Its crystal structure is shown in Fig. 4(a). The magnetism exhibited by magnetite is a result of the super-exchange interaction between the tetrahedral and octahedral sites, which yields magnetic moments that in both sublattices are antiparallel to each other. The distribution of iron within the spinel lattice is such that the magnetic moments of Fe$^{3+}$ (∼5 µB per atom) on both lattice sites cancel each other, resulting in a net magnetization due to Fe$^{2+}$ (∼4 µB per atom). The substitution of Fe$^{2+}$ or Fe$^{3+}$ cations in magnetite with transition metal dopants, such as cobalt, zinc, nickel or chromium, serves as a method in which to change the magnetic properties of the magnetic nanoparticles [66].

For an unambiguous determination of the relative site occupations in spinels and other ternary oxides, XMCD is the only available technique [12, 13]. The XMCD is dependent upon the magnetic moments of the Fe cation sublattice spinels in the magnetite structure (i.e., spin up and spin down), valence state (i.e., $d$ count) and site symmetry (crystal field). The distribution of Fe cations within the magnetite structure can be determined by comparison of the XMCD to atomic multiplet calculations [8, 25]. As shown in Fig. 4(b), each peak in the $L_3$ XMCD of Fe$_3$O$_4$ corresponds primarily to a different site in the magnetite, the first negative peak corresponds to octahedral Fe$^{2+}$, the second positive peak to tetrahedral Fe$^{3+}$ and the last negative peak to octahedral Fe$^{3+}$ [13]. In titanomagnetite (magnetite-ulvöspinel solid solutions) the XMCD contains furthermore an extra positive peak at the low energy side of the $L_3$ XMCD, which is due to tetrahedral Fe$^{2+}$ [67].

6.2. Bionanomagnetism

Bacterial surfaces can be used to pattern, template and scaffold metal nanocluster deposition, superseding chemical manufacturing for technologically important metal-based materials that are limited in several ways. Bacteria can also scavenge metals from liquid waste enzymatically, and perform nanofabrication of catalytic nanoparticles from precious metal
Figure 4. (a) Crystal structure of magnetite with octahedral (blue spheres) and tetrahedral (red spheres) sublattices and oxygen atoms (grey spheres). (b) Calculated multiplet structure of the XMCD for Fe $d^6$ $O_h$, Fe $d^5$ $T_d$ and Fe $d^5$ $O_h$, and the XMCD summed over the three sites for the stoichiometric composition $(\text{Fe}^{3+})[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$ [13].

The mechanisms of microbial metal reduction have been addressed with emphasis on the environmental impact and biotechnological application of Fe$^{3+}$-reducing bacteria [68, 69, 70]. A diversity of unrelated Fe$^{3+}$-reducing bacteria can convert ferrihydrite into the magnetic spinel magnetite. One of the long-term goals is to realize the biotechnological potential of anaerobic Fe$^{3+}$-reducing bacteria, by understanding and controlling their ability to produce nanocrystalline magnetic particles suitable for use with information management technologies. Successful development of these biomineralizing bacteria can revolutionize the manufacture of nanocrystals and provide low energy, environmentally friendly processing methodologies. In addition, this novel application of biotechnology has the potential to convert natural and waste Fe$^{3+}$ oxides that are bulky and difficult to handle, to a high value product that is easy to process.

The bio-produced spinels are ideally studied by XMCD, where the relative peak intensities of the three sharp peaks in the Fe $L_3$ XMCD with signature ($-,-,+,-$) are proportional to the site occupancies of the Fe$^{2+}$ ($d^6$ $O_h$), Fe$^{3+}$ ($d^5$ $T_d$) and Fe$^{3+}$ ($d^5$ $O_h$) cations, respectively [13]. Using XMCD the cation site occupancy of biogenic magnetite has been compared to polygenic ferrite spinels [71, 72]. XMCD has been successfully used to study the incorporation of vanadium [73], chromium [74, 75, 76, 77], manganese [78], cobalt [78, 79, 66], nickel [78], zinc [80], arsenic [81], technetium [75] and palladium [82] into the biomagnetite.

### 6.3. Reaction mapping

XMCD can be combined with scanning transmission x-ray microscopy (STXM) [83]. The combination of STXM and XMCD has been used to spatially resolve the distribution of different carbon and iron species associated with *Shewanella oneidensis* cells [84]. The bacteria couple the reduction of Fe$^{3+}$-oxyhydroxides to the oxidation of organic matter in order to conserve energy for growth. Findings suggest a dominant role for surface contact-mediated electron transfer in this study and also the inhomogeneity of magnetite species on the submicron scale present.
in microbial reactions. This also illustrates the applicability of this new synchrotron-based technique for high-resolution characterization of the microbe–mineral interface, which is pivotal in controlling the chemistry of the Earth’s critical zone.

7. Low-temperature physics
A very exciting and new area is low temperature physics with polarized soft x-rays. Magnetic, orbital and charge ordering phenomena are induced by rather weak interactions and usually only manifest at temperatures of a few Kelvin. This is currently the realm of neutron scattering. However, x-ray spectroscopies offer many advantages and the community now relying on neutron scattering will be able to take advantage of this new possibility to study, e.g., heavy-fermions, Kondo systems, frustrated magnets, and superconductors. The combination of low temperature and high magnetic field also allows the study of paramagnets and bioinorganic molecules of interest in the life sciences. The possibility to study magnetism under these extreme conditions using XMCD and XMLD will open up many interesting and unpredictable new avenues of research.

8. Magnetic imaging with coherent x-rays
8.1. Speckle patterns
Synchrotron radiation, like any other finite source, can be made coherent at the expense of flux, which means that a third-generation synchrotron source is able to produce a sufficient coherent flux [85]. The conditions for both longitudinal and transverse coherence have to be fulfilled. The longitudinal (or temporal) coherence length is determined by the resolving power of the monochromator at given wavelength. This condition is normally fulfilled because of the high energy resolution of the monochromator. The transverse (or spatial) coherence is obtained from the diffraction limit and depends on the distance and size of the source. The required transverse coherence can be achieved by spatial filtering, i.e., by inserting a pinhole with a diameter of typically a few tens of microns at close range in front of the sample. Finally, a charge-coupled device (CCD) camera is an essential requisite to record speckle patterns of the scattered radiation [86].

The speckle pattern is caused by the random path differences between radiation scattered from different locations in the sample irradiated with the coherent light, which interfere at the detector in the far field to produce an interference pattern [89]. The speckle pattern is sensitive to the particular configuration of the sample, whereas incoherent light scattering is only sensitive to statistical averages of the structure. To reconstruct the local configuration of the illuminated objects from the speckle pattern would require the measurement of the total signal (real and imaginary part), while only the intensity (i.e., the squared amplitude) can be detected and the phase is lost. So far only under very favorable circumstances, and for a small number of objects, the phase problem has been solved and the illuminated sample has been reconstructed directly from its coherent scattering pattern. However, progress has been made in this area by developing efficient algorithms and large computing power.

The presence of magnetic speckle, displaying a very high magnetic contrast, has opened up the possibility to use soft x-ray magnetic scattering for the study of static and dynamic magnetic disorder on length scales relevant for nanomagnetism [6, 90]. As an example, Fig. 5 shows the magnetic speckle from a FePd thin film with a perpendicular magnetic domain structure [91].

Combined with the time structure of synchrotron radiation, speckle measurements enable us to study rapid fluctuations in the local magnetic order, giving access to dynamical processes, and ultimately leading to improvements in the read-write speed of magnetic storage devices. This photon in—photon out technique allows us to study reversal processes as a function of magnetic field [91, 88, 92]. It enables to determine the degree to which the microscopic domain pattern is retained after magnetization cycling [93]. Since soft x-ray absorption spectra show a huge
magnetic dichroism compared to their hard x-ray counterparts, the magnetic peak intensities are more straightforward to analyse. With the advent of x-ray free electron lasers this new technique clearly holds great promises for the future of magnetic scattering, with imaging of dynamic disorder among the possibilities.

8.2. Magnetic imaging by x-ray holography
Fourier transform holography (FTH) is a well established lensless technique for imaging the perpendicular component of magnetic domains [94]. Holographic imaging, like x-ray scattering, is suitable not only for the remanent state [as typical for PEEM or magnetic force microscopy (MFM)] but can also be used under applied electric or magnetic fields and shows great potential for studying the dynamics of multiferroic thin films. A recent development in FTH has reduced the restriction on the reference size to allow a much wider range of possibilities. The technique, known as ‘holography with extended reference by autocorrelation linear differential operator’ (HERALDO) [95] permits the use of larger objects as references without compromising the spatial resolution. The HERALDO experiment is schematically displayed in Fig. 6 where it is used to image a Co/Pt multilayer with perpendicular magnetic domain structure [96].

9. Ferromagnetic resonance detected by XMCD
Ferromagnetic resonance (FMR) can be combined with XMCD to a technique called x-ray detected FMR (XFMR) [53, 98, 99, 100, 101]. XFMR offers unique element-specificity to probe the properties of multilayered films. Standard FMR cannot be used to study multilayer dynamics directly, since the signal is an average over the whole system. The precession frequency of the
Figure 6. Holography with extended reference by autocorrelation linear differential operator (HERALDO). (a) The object and reference slit are illuminated by a coherent x-ray beam. (b) The hologram formed by the interference of the scattered x-rays from the object and reference slit is recorded on the CCD camera in the far field. A linear differential filter, defined by the derivative of the slit direction, is multiplied by the hologram prior to performing a Fourier transform to retrieve the reconstructed image. (c) After Fourier transformation the image shows the out-of-plane magnetic domain structure of the object, in this case a [Co(5 Å)/Pt(10 Å)]×30 multilayer. Field-of-view = 1.5 μm and spatial resolution = 30 nm [96].

Figure 7. (a) Experimental geometry of x-ray ferromagnetic resonance (XFMR) experiment. The sample (pictured as the red disc) is mounted on the central strip of the coplanar waveguide (CPW). The magnetization $M(t)$ is forced into a state of steady precession about the applied bias field $H$ by an in-plane continuous microwave field $h(t)$ in the CPW. The circularly polarized x-ray pulses from the synchrotron are incident at grazing angle onto the sample in transverse geometry in order to detect stroboscopically the in-plane oscillatory component of the magnetization $M(t)$ at variable phase delay. (b) The dynamic XMCD signals at the Co and Ni $L_3$ edges from a MgO/NiFe(40 nm)/CoFe(40 nm) bilayer stack as a function of the delay time between the x-ray pulse and the phase of the microwave field. Shown is the high energy mode (the ‘optical resonance’) of the 9.5 GHz precession at $H = 65$ Oe, which shows that the Co and Ni magnetizations are precessing in anti-phase [97].
magnetization obtained by time-resolved XMCD measurements can be used to determine the magnetic parameters of magnetic thin films and nanostructures. These parameters include the internal dipolar field strength, the magnetocrystalline anisotropy constants, the exchange bias field, interlayer exchange coupling constants, the gyromagnetic ratio and the phenomenological damping constant.

The damping of the magnetization precession in thin films has been subject of extensive and vigorous debate with conflicting views about the correct functional form of the damping torque. The phenomenological damping is thought to arise from a combination of the following effects: intrinsic damping due to the spin-orbit interaction; eddy current damping; two magnon scattering from defects and impurities; dephasing of spin wave modes in confined geometries; and higher order spin wave processes. Transition metals can be doped with rare earths and different elements placed at the film interfaces to modify the damping.

The experimental set-up for XFMR is schematically illustrated in Fig. 7(a). The magnetization dynamics is driven by the microwave field of a coplanar waveguide (CPW). The oscillating current in the CPW generates a time-varying magnetic field that can be phase-locked to the x-ray pulses of the storage ring. A magnetic sample will absorb the microwaves of given frequency at the ferromagnetic resonance condition, resulting in a steady precession about the applied bias field. High sensitivity in FMR can be achieved using a vector network analyser (VNA), which can perform fast frequency sweeps. By sweeping both the microwave frequency and the applied field the resonances can be mapped. XMCD is sensitive to the magnetization component along the direction of the x-rays. Element specificity is obtained by tuning the photon energy to the absorption edge of the element of interest. Phase-resolved measurements of XFMR are made by varying the delay between x-ray pulse arrival and phase of excitation.

Applied to magnetic bilayers, multiple modes can be found describing the dynamics of the coupled layers, with a low and high energy mode corresponding to in-phase and anti-phase oscillation, respectively, between the layer magnetizations. XFMR in transverse geometry reveals for each mode the amplitudes and relative phase of the precessing magnetization in the adjacent layers. The phase delay between the microwave phase and the x-ray pulse for the high energy mode from a NiFe(40 nm)/CoFe(40 nm) bilayer is shown in Fig. 7(b).

10. Angular dependent measurements

10.1. Angular dependence in XMCD

For an isotropic system, which is magnetically saturated by an external field, the XMCD signal scales with the angle $\theta$ between the field and x-ray beam as $\cos \theta$ [34]. Consequently, in transverse geometry, i.e., perpendicular orientation of x rays and field ($\theta = 90^\circ$), the XMCD signal vanishes. In systems with cubic magnetic anisotropy, the XMCD spectrum is slightly different along ⟨001⟩ and ⟨111⟩ directions, due to the different symmetry of these axes ($C_4$ and $C_3$, respectively) [102]. The angular dependence of the intensity of the XMCD spectral features can be well described by the lowest order term for the cubic anisotropy [102].

The geometry of the XMCD experiment is described by three vectors, i.e., the light helicity, $\hat{P}$, the magnetization direction, $\hat{M}$, and the crystal frame orientation, $\hat{Z}$. For uniaxially distorted symmetry the XMCD signal can be decomposed as,

$$I_{\text{XMCD}} = I_0 \hat{P} \cdot \hat{M} + I_2 \left[ \frac{3}{2} (\hat{P} \cdot \hat{Z})(\hat{Z} \cdot \hat{M}) - \frac{1}{2} \hat{P} \cdot \hat{M} \right],$$  

where

$$I_0 = \frac{1}{3}(I_x + I_y + I_z),$$  

$$I_2 = \frac{2}{3}I_z - \frac{1}{3}(I_x + I_y),$$  

(2)
Figure 8. (a) Decomposition of the XMCD of an axially symmetric system into its isotropic and anisotropic contributions $I_0$ and $I_2$, respectively, where $\hat{z}$ is along the uniaxial direction. For the anisotropic XMCD the angular dependence is shown for $\hat{P} \perp \hat{M}$ [cf. Eq. (5)]. (b) Crystal structure of MnCr$_2$O$_4$.

are the isotropic and anisotropic XMCD contributions, respectively [34]. These have a simple graphical interpretation, as illustrated in Fig. 8(a).

In transverse geometry, where $\hat{P} \cdot \hat{M} = 0$, we obtain from Eq. (2) the angular dependence

$$I_{\text{XMCD}}(\hat{M}) = \frac{3}{4} I_2 \sin 2\nu = \frac{1}{2} (I_z - I_x) \sin 2\nu,$$

(5)

where $\nu = \angle(\hat{Z}, \hat{M})$ and taking $I_y = I_x$. The angular dependence of the anisotropic XMCD for $\hat{P} \perp \hat{M}$ is shown in Fig. 8. Therefore, in systems with axial magnetic anisotropy, such as uniaxial, tetragonal or trigonal symmetry of the lattice, a non-vanishing integral of the XMCD signal measured in transverse geometry corresponds to a non-zero component of the orbital magnetic moment perpendicular to the spin moment, a situation encountered in thin films with strong uniaxial magnetic anisotropy [103, 104].

The decomposition into isotropic and anisotropic parts can be applied—not only to the integrated $L_{2,3}$ intensities, i.e., sum rules—but also to the XMCD spectrum itself. XMCD measurements on MnCr$_2$O$_4$/SrTiO$_3$, with its crystal structure shown in Fig. 8(b), have revealed that the angular-dependent XMCD is strongly sensitive to strain-induced electronic structure variations [105]. This is a general phenomenon that provides an invaluable tool for studying and tailoring the physical characteristics of transition metal oxide nanoarchitectures through strain at interfaces of layered and nanocomposite heterostructures.

### 10.2. Angular Dependence in XMLD

In cubic crystals the XMLD depends strongly on the directions of the linear polarization, $\hat{E}$, and spin axis, $\hat{M}$, with respect to the crystallographic directions. A large anisotropy in the XMLD was first observed experimentally for the Mn$^{2+}$ $L_{2,3}$ edge in (Ga$_{1-x}$Mn$_x$)As, which was shown to be in agreement with atomic multiplet calculations [106]. This effect is also present in metallic systems, as was predicted by ab initio band structure calculations [107] and more recently observed in, e.g., Co-based Heusler alloys [108] and Ga$_x$Fe$_{1-x}$ [44].

The most intensively studied case is that of the antiferromagnetic NiO. The angular dependence of the XMLD at the Ni$^{2+}$ $L_{2,3}$ edges in a lattice with cubic symmetry can only be described as a linear combination of two fundamental spectra with distinctly different spectral
Figure 9. (a) Ni $L_{2,3}$ XAS and XMLD measured as the difference between the two local XAS spectra with in-plane linear x-ray polarization $\hat{E} \parallel [110]$. The two peaks of the $L_2$ edge, indicated by $A_1$ and $A_2$, have different magnetic contrast. (b) Multiplet calculations for the XMLD spectra $I_{45}$ and $I_0$ and the isotropic and anisotropic parts $\frac{1}{2}(I_0 + I_{45})$ and $\frac{1}{2}(I_0 - I_{45})$, respectively. The calculation shows that the $L_2$ XMLD contains only an anisotropic part. Right-hand side of the figure shows PEEM images of 2.5 nm Co/NiO(001) with field-of-view = 15 µm. (c) Ferromagnetic Co domains measured with circular polarization and (d) antiferromagnetic NiO domains measured with linear polarization. The polarization direction is indicated by the arrow in the bottom left corner of each panel. The other arrows indicate the deduced spin directions or axes of the different domains. In the Co XMCD PEEM image (c) the light and dark areas have the spin parallel and antiparallel to the light helicity vector, respectively. The grey areas in the Co image have the spin perpendicular to the light helicity. In the Ni XMLD PEEM image (d) the light and dark areas have their spin axis along [110] and [110], respectively. This means that the ferromagnetic Co and antiferromagnetic NiO layers are coupled perpendicular.

features [109, 26, 110, 111, 112]—and not just by a single spectrum as previously thought. Previous studies, such as by Alders et al. [113], Stöhr et al. [114] on NiO and Scholl et al. [115] on LaFeO$_3$, identified only a single XMLD spectrum.

The in-plane (001) XMLD spectra, defined as,

$$I_{\text{XMLD}} = I_{\text{XAS}}(\hat{E} \parallel \mathbf{M}) - I_{\text{XAS}}(\hat{E} \perp \mathbf{M}),$$

(6)

for $\hat{E} \parallel [100]$ and $\hat{E} \parallel [110]$ are indicated by $I_0$ and $I_{45}$, respectively. The subscript value denotes the angle between the linear polarization vector $\hat{E}$ with the [100] direction. The two fundamental spectra for the Ni$^{2+}$ $L_{2,3}$ XMLD in cubic symmetry are shown in Fig. 9(b). Comparison with
the calculated $I_0$ and $I_{45}$ spectra shows that at the $L_2$ edge, $I_{45} \approx -I_0$, whereas the $L_3$ structure is completely different. Therefore, to determine unambiguously the spin direction both the $L_2$ and $L_3$ structure need to be considered.

The $I_0$ and $I_{45}$ contributions have their maxima along $\langle 100 \rangle$ and $\langle 110 \rangle$, respectively [112]. Alternatively, one can decompose the XMLD into an ‘isotropic’ term, $\frac{1}{2}(I_0 + I_{45})$, which is rigidly coupled to $H$ and an ‘anisotropic’ term, $\frac{1}{2}(I_0 - I_{45})$, which is coupled to the crystal field frame [112].

XMLD-PEEM allows to determine the antiferromagnetic spin axes of magnetic domains. The spin coupling in Co/NiO(001) can be studied by comparing the PEEM images of ferromagnetic (FM) Co measured by XMCD [Fig. 9(c)] and antiferromagnetic (AFM) NiO measured by XMLD [Fig. 9(d)] [110, 111, 112]. Comparison of the spin directions unambiguously shows a perpendicular coupling between the FM Co and AFM NiO moments. Such a perpendicular coupling, which appears for certain Co thickness and interface roughness, was theoretically predicted by Koon [116] and later by Schulthess and Butler [117].

11. Conclusions
Different applications of x-ray magnetic dichroism have been summarized. The possibilities of magnetic dichroism in soft x-ray spectroscopy are vast and almost endless. XMCD and XMLD offer substantial advantages, such as element-specificity, spin and orbital moment analysis, magnetic anisotropy determination, magnetic imaging, surface sensitivity and time domain resolution. The technique provides a unique probe able to solve a large variety of different problems, such as the valency determination of the constituents in ternary oxides, the magnetic origin in dilute ferromagnetic semiconductors and the effects of electron correlation on the electronic structure.

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