We review some of the significant contributions to the field of strongly correlated materials and complex magnets, arising from experiments performed at the Diamond Light Source (Harwell Science and Innovation Campus, Didcot, UK) during the first few years of operation (2007–2014). We provide a comprehensive overview of Diamond research on topological insulators, multiferroics, complex oxides and magnetic nanostructures. Several experiments on ultrafast dynamics, magnetic imaging, photoemission electron microscopy, soft X-ray holography and resonant magnetic hard and soft X-ray scattering are described.

1. Introduction

Third-generation synchrotrons have become an essential tool to study a variety of crystalline materials, including strongly correlated systems and complex magnets; two fields that are closely linked with the work of British physicists Nevill Mott [1–3] and John Hubbard [4–6]. In strongly correlated materials, the Coulomb repulsion between electrons residing on the same atomic sites of the crystal is comparable to or greater than their kinetic energy. This has profound effects on the phenomenology of these materials, which can be very different from that of ordinary metals and insulators. In many materials, complex magnetism and exotic superconductivity develop in a context that is largely shaped by strong correlations.
Recently, a new class of materials with remarkable properties, known as topological insulators (TIs), has been at the centre of an international research effort. Although most TIs known to date are not strongly correlated, the two fields are closely connected by the similarity of the experimental techniques and by the proposal that topological effects and strong correlations could coexist, yielding a wealth of novel physics.

Nanomagnetism is another extremely important field of research with important technological ramifications. Although the basic physics and the classes of materials under investigation are quite distinct from either strongly correlated or topological materials, this area of research is linked to the other two by a commonality of research tools and, in some sense, paves the way for future technologies at the nanoscale employing more exotic materials.

These fields have become prominent in contemporary condensed matter research, thanks in no small part to the insights and contributions from X-ray and neutron facilities. In particular, a variety of diffraction and spectroscopic techniques have been developed at synchrotrons over the last three decades to study the crystal, electronic and magnetic structures of these materials.

In this paper, we review what we believe to be important contributions to this field of research arising from experiments performed at the Diamond Light Source over the first years of operation (2007–2014). The main purpose of this paper is to provide an overview of the work carried out at the available Diamond beamlines with a few sections devoted to a more detailed presentation of work carried out at the Nanoscience beamline (I06) covering ultrafast dynamics and magnetic imaging. Nevertheless, it is clearly impossible to give due credit to each and every individual piece of research, particularly for beamlines with a vast output in diverse fields such as the Powder Diffraction beamline (I11). We note, however, that synchrotron X-ray powder diffraction has become the tool of choice to determine subtle structural effects in samples synthesized de novo [7] or produced by high-pressure synthesis [8] or to study subtle structural phase transitions [9,10]. X-ray and neutron powder diffraction experiments together produce a powerful combination [11] while resonant X-ray powder diffraction has been used to generate site-selective contrast and determine cation ordering [12]. Unfortunately, on much of this work, we have to remain silent.

The paper is organized in topical sections covering areas of current interest in contemporary condensed-matter research such as TIs, multiferroics, complex oxides and nanomagnetism.

2. Topological insulators

A TI is a new type of quantum material that has attracted an enormous amount of interest, both theoretical and experimental, in recent years. Conceptually, a TI represents a new phase of matter and is distinct from an ordinary insulator by the topology of the electronic structure rather than by the symmetry, defying a paradigm which has served the condensed-matter physics community so well in the last century. A TI behaves like an ordinary insulator in the bulk, but possesses unusual electronic surface states in which momentum and spin are intimately correlated due to the spin–orbit (SO) interaction. These surface bands cross at special points of the Brillouin zone giving rise to features in the electronic dispersion known as Dirac cones, as quasi-particles at these locations behave like massless relativistic fermions. Unlike the case of ordinary insulators, the Dirac cones are topologically protected and cannot be destroyed by non-magnetic surface impurities. Moreover, non-spin-flip back scattering cannot occur in a TI, owing to the spin–momentum correlation, implying that the surface states have high mobility [13–16].

It has been predicted some time ago that small-gap semiconductors containing heavy elements could represent experimental realizations of a three-dimensional TI [17]. However, confirming this prediction from transport properties measurements has been problematic due to the difficulty in eliminating the contribution of the bulk states. The first experimental confirmations of TI behaviour were therefore produced from angle-resolved photoemission spectroscopy (ARPES) [18] and scanning tunnelling spectroscopy [19]. It is also no coincidence that the first publication from the ARPES beamline (I05) at Diamond is a report on the electronic
structure of a three-dimensional topological Dirac semimetal Cd₃As₂ [20]. In this paper, an Oxford–Stanford–Diamond group, led by Chen (Oxford), found that Cd₃As₂ possesses Dirac cones dispersing along all three crystallographic directions (figure 1), making it, in a sense, a three-dimensional analogue of graphene. Unlike other proposed materials, Cd₃As₂ is stable at ambient conditions and can be doped in situ, enabling control of the Fermi level.

Although the properties of massless Dirac fermions in the bulk and at surfaces are in themselves fascinating, it has been argued that a TI could display dramatic properties if the topological protection could be broken by introducing surface magnetism through doping. This would result in the opening of a gap at the Dirac points and in the Dirac fermions acquiring the equivalent of a mass. Special excitations, known as anyons, would appear at the walls between different magnetic domains. In addition, combining a TI with an ordinary superconductor leads to a correlated interface hosting exotic particles, known as Majorana fermions. Both anyons and Majorana fermions have been discussed as possible implementations of quantum computation at room temperature [21]. As a consequence, significant research effort has been devoted to producing and characterizing TI–superconductor interfaces and introducing magnetic impurities on TI surfaces in the hope of breaking time reversal symmetry and opening a gap in the surface states. At Diamond, a significant research effort has been devoted to magnetic surface doping of the prototypical material Bi₂Te₃. In particular, an Oxford–Diamond team employed growth by molecular beam epitaxy combined with X-ray magnetic circular dichroism (XMCD) on the Nanoscience beamline (I06). In this study, a perfect Bi₂Te₃ surface was implanted with Fe and Co adatoms at extremely low coverages (figure 2). Although the adatoms display a very large orbital moment, time reversal symmetry was found not to be broken [22]. The same group also doped Bi₂Te₃ in the bulk with Gd [23] and Mn [24], which are paramagnetic and ferromagnetic, respectively, at room temperature and characterized them with a variety of techniques including XMCD performed on the Nanoscience beamline (I06). Although the TI surface states are quite robust, determining the surface structure, and in particular the surface termination, of these materials is important, because structural relaxation can have dramatic effects on the electronic structure. Dos Reis and co-workers studied in detail the surface structure of another prototypical TI, Bi₂Se₃, employing low-energy electron diffraction and surface X-ray diffraction on the Surface

Figure 1. (a) The topology of the three-dimensional Dirac cone (a four-dimensional object) in Cd₃As₂ (from [20]). (b) Schematic of the three-dimensional Dirac cone projected onto (kₓ, kᵧ, E). (c) Schematic of the three-dimensional Dirac cone projected onto (kᵧ, kₒ, E). The data (shown in the bottom row) are from the ARPES beamline (I05). (Online version in colour.)
and Interface Diffraction beamline (I07) and concluded that the crystal is terminated by an intact ‘Se–Bi–Se–Bi–Se’ quintuple layer [25].

Besides small-gap binary semiconductors, several other candidates have been proposed as candidates for TI behaviour, most notably heavy transition metal oxides [26]. A particularly interesting study was performed on the Small Molecule Single-Crystal Diffraction beamline (I19) to determine the crystal structure of one of the most exotic candidates, the molecular kagomé compound (EDT-TTF-CONH₂)₆[Re₆Se₈(CN)₆] [27]. Band structure calculations based on the experimental crystal structures predict the presence of topologically protected Dirac cones at the Fermi surface, similar to those of graphene.

3. Multiferroics

(a) Introduction to multiferroics

Multiferroics form a subset of ferroelectrics, in which long-range magnetism can coexist with, and couple to ferroelectricity. These materials have been studied since the 1960s, but have recently received significant attention because a wave of new discoveries has led many to believe that relatively strong coupling effects could be obtained at room temperature. This would be extremely appealing since controlling magnetic states with electric fields could lead to a new generation of low-power, non-volatile memory devices [28]. The following classification has been proposed for multiferroics: type I multiferroics undergo an ordinary structural, non-polar to polar phase transition (usually involving the breaking of inversion symmetry) leading to ferroelectricity at high temperatures, while magnetic order develops during a separate phase transition at lower temperatures. In type II multiferroics the staggered (antiferromagnetic) magnetization is the primary order parameter. Magnetic ordering below a given temperature lowers the symmetry group from a non-polar parent phase to a polar magnetic phase. Magneto-structural coupling to the crystal structure then gives rise to an electrically polar state inducing improper ferroelectricity. In this case, magnetic and ferroelectric order parameters are closely (and usually strongly) coupled. However, type II multiferroicity is usually found at low temperatures, owing to the inherent magnetic frustration required to generate acentric magnetic structures and produce weak electric polarizations.
The rebirth of the field of multiferroics is usually traced back to 2003, when Kimura et al. [29] demonstrated the magnetic field control of electric polarization ‘flopping’ in TbMnO$_3$. Ever since, advanced X-ray scattering techniques have played a major role in the field, with many important experiments having been performed at Diamond. Advanced synchrotron X-ray diffraction experiments may be performed to investigate the most subtle changes in crystal structure due to magnetoelastic interactions. Moreover, with the advent of high brilliance third-generation synchrotron sources, it is now possible to diffract X-rays directly from ordered magnetic moments within the sample through interaction with the magnetic part of the electromagnetic radiation or by exploiting resonance effects. The revival of multiferroics has also produced a resurgence of interest in related magnetoelectric materials, which, unlike multiferroics, do not possess a spontaneous polarization. Several experiments concerning magnetoelectrics have been performed at Diamond, for example in [30,31].

The coupling of magnetic and structural degrees of freedom is, unfortunately, rare so that new avenues for realizing such materials involve artificial structures that exploit the relevant phase transitions in each component part of the structure. Moya et al. (Cambridge) have realized such a structure using a thin film of La$_{0.7}$Ca$_{0.3}$MnO$_3$ grown on a BaTiO$_3$ substrate. In this case, by controlling the magnetic structure of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ via strain during a structural phase transition in the BaTiO$_3$ substrate, very large entropic and reversible changes were realized in the material. This remarkable result is discussed in the final part of this section.

(b) Type I multiferroics

Type I multiferroics are intensely studied because several examples are known of magnetic materials with good ferroelectric properties at room temperature. By far the most interesting is BiFeO$_3$ since it is magnetic above room temperature and therefore potentially suitable for applications. BiFeO$_3$ is a rhombohedrally distorted perovskite, in which electrical polarization develops at $T_C \sim 1100$ K along the hexagonal $\langle 001 \rangle$ directions (corresponding to pseudo-cubic $\langle 111 \rangle$ directions) due to the presence of a Bi lone pair. In bulk samples, the magnetic ordering transition occurs at $T_N \sim 640$ K. Locally, the magnetic structure is that of a simple G-type antiferromagnet, but Dzyaloshinsky–Moriya (D-M) interactions promote the formation of a long-period (approx. 640 Å) cycloidal rotation of the spins in a plane containing the polar direction as well as of local weak ferromagnetism. In a cycloidal magnetic structure, spins rotate in a plane that contains the direction of propagation. Understanding the interplay between ferroelectric and magnetic domains is, however, essential to control device functionality. For each polar direction (along the $\langle 001 \rangle$ hexagonal direction), three magnetic cycloidal domains can be present, with propagation vectors $k_1 = 2\pi (\delta, \delta, 0)$, $k_2 = 2\pi (\delta, -2\delta, 0)$ and $k_3 = 2\pi (-2\delta, \delta, 0)$ in the hexagonal setting. Johnson et al. (in the group led by Radaelli) imaged these magnetic domains directly on the surface of a single-domain polar BiFeO$_3$ crystal using non-resonant magnetic X-ray diffraction [32] on the Materials and Magnetism beamline (I16). This challenging experiment highlights the excellent quality of the Diamond beams and of this beamline in particular: the observed magnetic Bragg peaks, typically eight orders of magnitude weaker than the structural (charge) Bragg peaks, are crowded around the $\langle 009 \rangle$ reciprocal space position. Although the $\langle 009 \rangle$ reflection is forbidden, multiple scattering processes can give rise to charge scattering at this position, and the magnetic contribution needs to be carefully separated out by means of high resolution and a careful selection of the scattering conditions. Data were then acquired by defining surface pixels using a small (down to $10 \times 25 \mu \text{m}^2$) incident X-ray beam, and the whole crystal surface was imaged by scanning the position of the crystal (figure 3). The absolute direction of rotation of the cycloids was also determined using circular dichroic scattering. The magnetic domains were found to be rather large (several hundred micrometres) and the magnetic cycloids in each domain were found to propagate with a unique rotation direction imposed by the electric polarity of the crystal. The experimentally determined rotation direction is found to be consistent with density-functional simulations, highlighting the increasing importance of modelling for the interpretation of a variety of synchrotron experiments.
Figure 3. (a) A picture of the BiFeO$_3$ crystal used for the first non-resonant magnetic scattering experiment on the Materials and Magnetism beam line (I16). (b) Magnetic domain imaging on the surface of the crystal, collected with a resolution of 50 × 50 µm. Each of the three colour (shades) represents a distinct magnetic domain (from [32]). (c) Data collected on a larger crystal with a resolution of 10 × 25 µm (unpublished data). The black lines show the outline of lozenge-shaped domains in the middle of the crystal. (Online version in colour.)

The canonical model of magnetism in BiFeO$_3$ is described in terms of circular cycloids propagating in a direction perpendicular to the electrical polarization. The magnetic structure has a polarity but does not possess chirality. Very recent experiments, also performed on the Materials and Magnetism beamline (I16), by Rodriguez-Fernandez et al. [33], suggest that the magnetic structure may be more complex, with charge-like quadrupoles and hexadecapoles as well as ordinary magnetic dipoles participating in a circular cycloid. The structure proposed by Rodriguez-Fernandez et al. would be chiral as well as polar, with the chirality persisting also above the Néel ordering temperature.

(c) Type II multiferroics

Type II multiferroics have proved to be an extremely fertile field of study for X-ray synchrotron techniques. The propagation vectors of their magnetic structures are always well away from the zone centre, so that magnetic Bragg peaks are readily observed with X-rays in both resonant and very often non-resonant conditions for good-quality single crystals. In most cases, the magnetic structures of type II multiferroics have been studied by neutron diffraction for some time and long before their multiferroic properties were known. However, more recent studies with both neutrons and X-rays have revealed unexpected subtleties which are often crucial in the understanding of the correlation between magnetic ordering and multiferroicity. An extended review of the diffraction studies of type II multiferroics is presented in [34].
TbMnO$_3$ is the prototypical type II multiferroic. The magnetic structure of TbMnO$_3$ was first reported in 1977 by Quezel et al. [35]. Analysis of neutron powder diffraction data showed evidence of long-range, antiferromagnetic ordering below $T_N = 40$ K, with an incommensurate modulation propagating parallel to the $b$-axis (in the $Pbnm$ setting), $(0,q,0)$ with $q \approx 0.295$, which then locks at $q \approx 0.28$ below $T_{lock} = 30$ K. The study concluded that the magnetic structure was formed of sinusoidally varying magnetic moments located on the manganese sites, which were also aligned along the $b$-axis. Following the discovery by Kimura of magnetically induced electrical polarization below $T_{lock}$, the details of the magnetic structure in the polar phase were established by Kenzelmann et al. by neutron scattering [36]. Kenzelmann et al. found that, in the polar phase, the magnetic moments rotated in the $bc$-plane forming a transverse, short period cycloid. Unlike the case of BiFeO$_3$, the cycloid is induced by competition between nearest-neighbour and next-nearest neighbour Heisenberg-exchange interactions which induce the electrical polarization through the so-called inverse D-M mechanism rather than being induced by a pre-existing polarization. More generally, the inverse D-M mechanism provides an explanation for the appearance of electrical polarization in many cycloidal magnets [37,38]. Among the numerous subsequent synchrotron X-ray studies on TbMnO$_3$ and related compounds in the RMnO$_3$ series ($R =$ Tb, Dy and Gd, see again [34] for a complete review) the work by Fabrizi et al. [39], working at the European Synchrotron Radiation Facility (ESRF) with a group led by McMorrow (University College London), is particularly noteworthy. Fabrizi et al. demonstrated for the first time that the absolute direction of rotation of the magnetic structure, which is completely equivalent to the magnetic polarity, can be unambiguously determined by magnetic scattering of circularly polarized X-rays. Although neutron spherical polarimetry (NSP) is an alternative technique to obtain this information, X-rays have many advantages: first of all, X-ray measurements can be performed in applied magnetic as well as electric fields, whereas NSP is strictly a zero-magnetic-field technique. Moreover, the X-ray beam can be focused down to a few micrometres, making this techniques suitable to image magnetic polarity domains (also known as chirality domains for historical reasons), whereas NSP is more suitable to determine domain populations in the bulk. The power of X-ray magnetic scattering to image magnetic domains was later demonstrated by the same group on the type II multiferroic Ni$_3$V$_2$O$_8$ [40], which also possesses a cycloidal magnetic structure.

CuO is a particularly important example of cycloidal magnetism, because of the simplicity of the chemical and crystal structures and because the multiferroic behaviour is displayed at rather high temperatures (213–230 K). The study of magnetism in this simple model compound can also have important implications for the understanding of high-temperature superconductors, to which CuO is chemically and structurally related. An experiment performed at the ESRF and at the Swiss Light Source by Scagnoli et al. [41], but with a crucial theory contribution from Diamond scientists, seems to show evidence of such a link. Scagnoli et al. used resonant X-ray diffraction to observe the so-called orbital currents in a copper–oxygen plaquette, the basic building block of cuprate superconductors.

Many other type II multiferroics have complex rotating magnetic structures but do not fall neatly in the category of cycloidal magnets. Cu$_3$Nb$_2$O$_8$, which was studied by Johnson et al. [42] on the Materials and Magnetism beamline (I16), provides just such an example. Below 24 K, Cu$_3$Nb$_2$O$_8$ spins order with helicoidal magnetic structure of the most general kind. Johnson et al. demonstrated that the direction of polarization in Cu$_3$Nb$_2$O$_8$ is inconsistent with the cycloidal mechanism and proposed a new ‘ferroaxial’ mechanism that couples with the chiral component of the magnetic structure. It is noteworthy that Cu$^{2+}$ ions in this compound have $S = \frac{1}{2}$. The fact that such detailed information could be extracted in a system with such low spin using non-resonant scattering is a remarkable testimony to the quality of the data produced by the Materials and Magnetism beamline (I16).

Resonant soft X-ray diffraction (RSXD) is another powerful tool to study multiferroics, although, in the case of transition metal oxides, its applicability is limited to materials where magnetic Bragg peaks are present in the Ewald sphere accessible at the $L_{2,3}$, $M_{4,5}$ or O K-edge resonances [43]. Nevertheless, significant insights have been obtained using RSXD [44–46], and
RSXD is also an area of active interest for Diamond theorists [47–50]. A good example is provided by the so-called hexaferrites. There are three main types of hexaferrites relevant to the study of magneto-electricity. The most significant are known as M-type, Y-type and Z-type, with respective general chemical formulae $A\text{Fe}_{12}\text{O}_{19}$, $A\text{Z}_{2}\text{Fe}_{12}\text{O}_{22}$ and $A\text{M}_{2}\text{Fe}_{24}\text{O}_{41}$ (where, for example, $A$ = Pb, Ca, Sr, Ba and $M$ is a transition metal ion). Hexaferrites are particularly interesting because they are magnetic and in some cases multiferroic at room temperature. For a full description of their electrical and magnetic properties, we defer to a comprehensive review by Kimura [51]. Many hexaferrites, such as the Y-type $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$, have proper-screw (helical) magnetic structure, in which spins rotate in a plane perpendicular to the direction of propagation. Electrical polarization develops upon application of a small magnetic field in an appropriate direction, owing to a variant of the inverse D-M mechanism. The effect of the field is to convert the structure from helical to conical and to tilt the axis of the cones, inducing a small cycloidal component [52]. $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2}\text{Fe}_{12}\text{O}_{22}$, also Y-type, is a peculiar and not yet completely understood case so that it has been the subject of several experiments at Diamond. The zero-magnetic-field magnetic structure is a simple helix with propagation along the $c$-axis of the hexagonal crystal structure. However, application of a small magnetic field perpendicular to the $c$-axis does not result in a conical structure, but in a so-called fan structure, where the spin oscillates around the magnetic field direction with definite periodicity. Hearmon et al. performed a series of resonant soft-X-ray experiments on $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2}\text{Fe}_{12}\text{O}_{22}$, using the Nanoscience beamline (I06) [53] and the beamline for advanced dichroism experiments (I10) [54]. They discovered an intricate hierarchy of fan structures at low magnetic fields, resulting from a subtle competition of exchange interactions, before the system enters the acentric polar phase. A key to the success of these experiments was the new reflectivity and advanced scattering from ordered regimes (RASOR) diffractometer installed on I10 [55] which is capable of excellent resolution and reproducibility.

Type II multiferroicity can also be found in collinear or quasi-collinear magnetic structures. The $\text{R Mn}_2\text{O}_5$ family ($\text{R} = \text{La, Y, Bi or rare earth element}$) with the orthorhombic space group $Pbam$ provides excellent examples of quasi-collinear multiferroics, many of which were extensively studied on the Materials and Magnetism beamline (I16) [56–58]. Through these studies, taken in combination with neutron scattering experiments, it was possible to establish that ferroelectricity in these materials arises almost entirely from a completely different mechanism, the so-called symmetric exchange striction [59]. Here, a key advantage was the ability to use a combination of non-resonant and resonant magnetic scattering to disentangle the separate contributions of the rare earth and Mn to the magnetic structures. As they become magnetically ordered, these materials develop tiny structural distortions, which are not related to the electrical polarization, involving displacements as low as a few tens of femtometres. Remarkably, it was possible not only to observe the charge Bragg peaks arising from these distortions [56], but also to obtain a full structural refinement of the displacement parameters [58]. In this context, it is worth mentioning the remarkable experiment performed at the ESRF by Walker et al., which observed femtoscale magnetically induced lattice distortions in $\text{TbMnO}_3$ by exploiting interference effects between charge and magnetic scattering.

The potential of other Diamond beamlines to study the interplay between structure and magnetism has perhaps not been fully explored to date. A detailed study of the helical diffuse scattering resulting from electronic textures in the candidate multiferroic $\text{YbFe}_2\text{O}_4$ [60] has been performed on the Small Molecule Single-Crystal Diffraction beamline (I19) [61]. Several experiments on a variety of multiferroics, mainly to characterize the crystal structure [62–64] or to study structural phase transitions [65–67] were also performed on the Powder Diffraction beamline (I11) [68].

(d) Giant magnetocaloric effects in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{BaTiO}_3$

Magnetocaloric effects have been studied since the nineteenth century, but two breakthroughs over 100 years after their discovery sparked a renaissance in the field. The first was the development of a viable magnetic refrigerator [69] followed by the discovery of a giant
Figure 4. Photoemission electron microscopy (PEEM) vector maps of the La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ film magnetization taken at (a) approximately 150 K and (b) approximately 210 K, imaged with XMCD contrast. The colour wheel indicates the direction of the magnetization. The magnitude information alone is shown in (c,d), where red (grey) contours enclose regions with very low XMCD asymmetry and thus zero magnetization within error. (e) Average XMCD asymmetry versus temperature obtained from (c,d) for the whole of each image (open circles) and regions with XMCD asymmetry greater than 0.015 (filled circles). The filled circles with solid line represent the magnetization recorded using VSM. (Online version in colour.)

The magnetocaloric effect in Gd$_5$Si$_2$Ge$_2$ [70]. These giant magnetocaloric effects are quantified by isothermal changes in entropy during spontaneous magnetic ordering when accompanied by a concomitant change in the crystal symmetry or volume. However, such a coupling of the magnetic and structural degrees of freedom is rare so that there is now active interest in engineering magnetocaloric effects using, for instance, strain. Moya et al. [71] have discovered that La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films grown on BaTiO$_3$ substrates exhibit a giant and reversible magnetocaloric effect, with a value approaching that obtained for Gd$_5$(Si$_1$Ge$_2$), which is novel since the intrinsic effect reported for bulk La$_{0.7}$Ca$_{0.3}$MnO$_3$ is relatively small [72]. The effect arises at the BaTiO$_3$ rhombohedral–orthorhombic (R–O) structural phase transition which induces strain at the La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ interface resulting in entropic ferromagnetic–paramagnetic phase conversion characterized by a hysteretic jump in the magnetization as a function of temperature. The giant effects in the presence of a magnetic field are considered to progress via a strain-mediated feedback mechanism, but at Diamond Moya et al. concentrated on the microscopic origin of the effect by imaging regions of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ film that undergo a ferromagnetic–paramagnetic phase change with temperature.

Photoemission electron microscopy (PEEM) combined with XMCD is a powerful elementspecific probe of the local magnetization with a resolution in the range of approximately 50 nm. The intensity in a PEEM image recorded with XMCD contrast is proportional to the projection of the local magnetization vector onto the polarization vector of the incident X-ray beam making it an ideal probe of nanoscale magnetic domain structures [73]. In addition, by combining PEEM images recorded at two different sample orientations, while keeping the incident beam direction fixed, magnetization vector images can reveal changes in the magnitude and direction of the local magnetization during a phase transition. Figure 4 shows vector images of the local in-plane magnetization from a La$_{0.7}$Ca$_{0.3}$MnO$_3$ film recorded at the Mn L$_3$ edge below (approx. 150 K) and above (approx. 210 K) the substrate R–O phase transition at
approximately 200 K. The magnetization in the PEEM images is highly inhomogeneous, but its average value, determined from the entire field of view of many PEEM images, follows closely $M(T)$ in figure 4d demonstrating that the phase separation arises due to inhomogeneous strain from the substrate. Specifically, after warming to approximately 210 K across the R–O transition large black areas (bounded by the red (grey) lines) appear in figure 4d indicating a growth of paramagnetic areas at the expense of ferromagnetic areas. The zero-magnetization regions occupy areal fractions of 8% at approximately 150 K and 43% at approximately 210 K. The magnetization (extracted from the PEEM images) with temperature is shown in figure 4e. The solid black circles, representing only the magnetic areas, track the background slope of the bulk magnetization (determined using vibrating sample magnetometry (VSM)), while the extracted magnetization of the entire field-of-view accurately follows the step in the bulk magnetization. The PEEM analysis therefore implies that the ferromagnetic–paramagnetic phase interconversion is responsible for the jump in the magnetization and hence the entropic changes. The magnetic phase separation arises due to the rotation of the MnO$_6$ octahedra promoting localization of charge carriers and inhibiting ferromagnetic metallic interactions. Although the changes discussed above were driven thermally, they can also be driven using a magnetic field which yields magnetocaloric effects of $-9\text{ JK}^{-1}\text{ kg}^{-1}\text{ T}^{-1}$ for La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ compared with $-0.9\text{ JK}^{-1}\text{ kg}^{-1}\text{ T}^{-1}$ for bulk La$_{0.7}$Ca$_{0.3}$MnO$_3$ [72] and $-3.7\text{ JK}^{-1}\text{ kg}^{-1}\text{ T}^{-1}$ for Gd$_5$Si$_2$Ge$_2$ [70].

The insights that PEEM combined with XMCD or X-ray magnetic linear dichroism yield are important where multiple phases exist simultaneously leading to electronic phase separation which is widespread in transition metal oxides. Low-temperature aberration corrected PEEM should allow unprecedented insights into competing orders in highly correlated materials. Recent results from the aberration-corrected PEEM instrument at the Advanced Light Source, USA [74], combined with RSXD, reveal a complex behaviour for phase separation in La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ between ferromagnetic, orbitally ordered, charge-ordered and antiferromagnetic domains. The ferromagnetic domains are found to nucleate under the strain introduced by the charge, orbital and antiferromagnetic ordering with temperature-dependent imaging of the ferromagnetic domains suggesting a glassy behaviour that competes with ferromagnetic metallic order to drive the phase separation.

4. Complex oxides

(a) Iridates

Transition metal oxides of the 5d group have recently attracted attention as candidates to exhibit novel electronic ground states stabilized by the strong SO coupling, including topological band- or Mott-insulators, quantum spin liquids, field-induced topological order, topological superconductors and spin-orbital Mott insulators [75]. One of the most prominent features of these compounds is the presence of composite spin–orbital moments coupled via frustrated exchanges. Within this family of compounds, iridates with an Ir$^{4+}$ oxidation state (5d$^5$ electronic configuration) have received particular attention. Here, the SO coupling is predicted to lift the degeneracy of the t$_{2g}$ states, resulting in $J_{\text{eff}} = \frac{1}{2}$ spin–orbital composite states (‘isospins’). The coupling between such states on a lattice is often represented by very unusual Hamiltonians. For example, Kitaev has shown that a honeycomb arrangement of the ions is associated with a highly anisotropic exchange Hamiltonian, with an exactly soluble quantum spin liquid ground state. It has been proposed that the hexagonal iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$, which possess layered structures consisting of a honeycomb lattice of Ir$^{4+}$ ions, could be experimental realizations of this model. Much of the experimental effort has focused on the attempt to confirm the existence of the $J_{\text{eff}} = \frac{1}{2}$ state in Ir$^{4+}$ compounds and on the study of the magnetic isospin ground states and their excitations, although, up to now, Kitaev physics remains somewhat elusive. Resonant elastic (REXS) and inelastic (RIXS) scattering are ideal tools to study iridium compounds: experiments are usually performed at the Ir L$_3$ and L$_2$ edges (approx. 11.2 keV and approx. 12.8 keV) where resonant enhancements are strong. Ewald spheres are large and experimental geometries are
relatively simple. By contrast, neutron scattering on these compounds is problematic because of the strong absorption from Ir. Early work on iridates includes some spectacular RIXS data by Kim et al. [76] showing isospin magnon dispersion in Sr$_2$IrO$_4$ and by Hill et al. [77] who determined a long-range magnetic ordering in Na$_2$IrO$_3$. At Diamond, much of the work on iridates has been carried out on the Materials and Magnetism beamline (I16) by the group of McMorrow, focusing on the single-layer (Sr$_2$IrO$_4$, Ba$_2$IrO$_4$) and double-layer (Sr$_3$Ir$_2$O$_7$) Ruddlesden–Popper phases. Similar to the previous work of Hill et al., Boseggia et al. [78,79] determined the magnetic structure of Sr$_3$Ir$_2$O$_7$ by REXS and also imaged the magnetic domains, which were found to be of the order of 100 µm. The work of the McMorrow group on the single-layer materials focused on exploring the robustness of the conclusion that these systems are representative of the $J_{\text{eff}} = \frac{1}{2}$ state, traditionally inferred from the $L_2/L_3$ branching ratio for different spin directions and in the presence of significant lattice distortions [80,81]. One important result they obtained is that the possibility of observing the $J_{\text{eff}} = \frac{1}{2}$ state by REXS is limited to specific states, i.e. when the moment is parallel to the c-axis.

(b) Charge and orbitally ordered oxides

Synchrotron techniques have been used for many years to study charge and orbital ordering in transition metal oxides. These phenomena involve the spontaneous ordering of distinct valence states of the same species, usually a transition metal atom (charge ordering), often accompanied by the preferential occupation of certain orbitals, forming a regular pattern throughout the crystal (orbital ordering). In most cases, the orbital degeneracy is lifted by the cooperative Jahn–Teller effect. In the early 1950s, Goodenough deduced the presence of charge and orbital ordering in the manganese perovskite La$_{0.5}$Ca$_{0.5}$MnO$_3$ [82], based on the analysis of the unusual magnetic ordering patterns which had been determined by neutron diffraction shortly before. However, a confirmation of this prediction remained elusive for many years. There are two ways to confirm this conjecture experimentally: one could use synchrotron crystallography to look at the subtle distortion of the lattice and of the atomic arrangement, arising from charge/orbital ordering—an approach that is often considered somewhat indirect. Alternatively, one can employ techniques such as REXS which is directly sensitive to both valence and orbital occupation through the so-called anisotropy of the tensor of susceptibility, i.e. the anisotropy of the scattering cross section for different orientation of the X-ray polarization. The first observation of charge and orbital ordering in La$_{0.5}$Ca$_{0.5}$MnO$_3$, confirming the Goodenough prediction, was obtained by non-resonant synchrotron X-ray diffraction [83]. Later, several experiments by Murakami et al. reported the ‘direct’ observation by REXS of orbital ordering on the end member of the perovskite family, LaMnO$_3$ [84], and of charge and orbital ordering in the related single-layer compound La$_{0.5}$Sr$_{1.5}$MnO$_4$ [85]. Although the interpretation of these data is far less straightforward than the one given by Murakami et al. [86], this tool has become established in the study not only of manganites, but also of other transition metal oxides with similar phenomenology. Although the experiments of Murakami et al. were performed at the Mn K-edge, it is usually better to employ soft X-ray scattering at the $L_{2,3}$-edges (640–650 eV) which probes transitions directly into the relevant d electronic orbitals. This is, however, not possible for all materials, since the Ewald sphere is small and only Bragg peaks at relatively large spacings can be observed.

At Diamond, the group of Hatton (Durham) employed this technique to study the bilayer manganite compound Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$ [87,88]. Experiments were performed at the Mn $L_{2,3}$ edges on the Nanoscience beamline (I06). It has been previously determined that, in this material, the occupied orbitals form stripes running along the a-axis and that the stripe pattern is destroyed upon warming above 370 K. The main conclusion of this study was the observation of a rotation of the stripe pattern from the a-axis to the b-axis direction upon cooling below 300 K.

Charge and orbital ordering phenomena are not limited to manganites and have been found to play a prominent role, for instance, in the phenomenology of cuprate superconductors and also of nickelates and cobaltates with related crystal structures. One interesting example, which was studied in detail on the Materials and Magnetism beamline (I16) by a group led by...
Coldea (Oxford), is that of the hexagonal AgNiO₂ nickelate [89]. AgNiO₂ has several unusual features which were previously explored by the same group using neutron diffraction and other techniques [89,90]. The most significant feature is that, unlike the case for other isostructural and isoelectronic nickelates such as NaNiO₂, the Jahn–Teller mechanism does not seem to be active in AgNiO₂ so that it remains hexagonal and metallic at all temperatures. Nevertheless, a structural distortion between two hexagonal phases does take place in AgNiO₂ below 340 K, followed, on cooling, by magnetic ordering at approximately 20 K. Neutron scattering from both crystals and magnetic structures could be interpreted in terms of charge disproportionation whereby two different valence states of Ni (2⁺ and 3.5⁺) are simultaneously present in the crystal (in a 1:2 ratio) adding up to the nominal Ni³⁺ valence. Charge ordering of the two species on different crystallographic sites then leads to spin ordering, at lower temperatures, of the magnetic Ni²⁺ ions. This would represent a novel way to lift orbital degeneracy, alternative to the usual Jahn–Teller mechanism. The work carried out at the Materials and Magnetism beamline (I16) was seeking a direct confirmation of this picture to corroborate the previous indirect observations through crystallography and magnetic scattering. REXS data shown in figure 5 were collected at the Ni K-edge (approx. 8.45 keV) on a tiny single crystal (approx. 50 µm in size) extracted from a powder batch. As we have already mentioned, the interpretation of K-edge data is far from straightforward so that several Bragg peaks were measured and the spectra were carefully
corrected for attenuation before extracting the real and imaginary parts of the anomalous atomic scattering factors for the two distinct crystallographic sites. These were then modelled on the basis of first-principle calculations, carried out in the local density approximation, so that the valence states of the two sites could be determined. The edge shift of approximately 2.5 eV between the two sites was found to correspond to a disproportionation of approximately 1.65 electrons in very good agreement with the expected Ni$^{2+}$ and Ni$^{3.5+}$ charge ordering scenario.

### (c) Photomelting of antiferromagnetic order

Competition between charge, spin and orbital ordering in transition metal oxides is a common feature of strongly correlated materials and is fundamental to phenomena such as high-$T_c$ superconductivity and colossal magnetoresistance. The interest in these materials arises due to the small energy difference between different phases that develop upon doping so that pressure, magnetic fields and light can be used to reversibly switch from one phase to another. The group of Cavalleri (Oxford and Centre for Free-Electron Lasers, Hamburg) along with Dhesi (Diamond Light Source) developed time-resolved soft X-ray diffraction on the Nanoscience beamline (I06) to study the single-layered manganite La$_{0.5}$Sr$_{1.5}$MnO$_4$ [91,92]. This material undergoes a metal–insulator transition at approximately 240 K resulting in charge and orbital ordering in the MnO$_2$ planes. Concomitantly, a complex spin ordering with antiferromagnetically coupled ferromagnetic zigzag chains develops in the MnO$_2$ layers. Upon lowering the temperature further to approximately 110 K the material becomes a CE type antiferromagnet [93].

RSXD is sensitive to spin and orbital ordering in manganites through 2p $\rightarrow$ 3d dipole transitions at the Mn $L_{2,3}$ edges. Furthermore, the energy dependence of the diffraction peak intensity can be used to understand the interactions responsible for spin and orbital ordering [94–99]. The extension of RSXD into the ultrafast regime employs a pump–probe approach combining optical excitation with an X-ray probe. Time-resolved RSXD then becomes a unique probe to understand non-equilibrium states in which spin, charge or orbital ordering can be modified. RSXD was used on the Nanoscience beamline (I06) to study the ultrafast spin and orbital dynamics in La$_{0.5}$Sr$_{1.5}$MnO$_4$. The intensities of the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{1}{4}, 0)$ diffraction peaks, related to spin-ordering and orbital ordering, respectively, were studied following excitation with an 800 nm laser pulse [91]. By following the dynamics of the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{1}{4}, 0)$ diffraction peaks in the time domain, it was possible to separate the evolution of both the magnetic and orbital degrees of freedom following photoexcitation.

**Figure 6a, b** shows the time dependence of the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{1}{4}, 0)$ diffraction peaks recorded at 640.25 eV and 641.5 eV, respectively, following photoexcitation using an 800 nm laser pulse. **Figure 6c, d** shows the energy dependence of the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{1}{4}, 0)$ diffraction peaks 200 ps after the laser pump pulse. The results show that, above a fluence of 5 mJ cm$^{-2}$, a new photoinduced non-equilibrium phase can be created in which the magnetic ordering is completely suppressed, but the orbital ordering remains largely intact. The CE phase is subsequently reconstructed over several hundred nanoseconds after photoexcitation which is too slow to be a result of thermal diffusion. Instead, the excited state is considered to relax across a kinetic barrier requiring domain growth and nucleation of the CE phase. Ultrafast RSXD therefore shows that photoexcitation destabilizes the short-range exchange pattern with very little influence on the long-range Jahn–Teller distortions. The photoexcitation process transfers electrons between the Mn$^{3+}$ and Mn$^{4+}$ ferromagnetically coupled sites resulting in charge defects puncturing the zigzag ferromagnetic chains. This significantly disrupts the exchange pattern so that, according to the Goodenough–Kanamori–Anderson rules, antiferromagnetic coupling can be introduced into the ferromagnetic zigzag chains. The long-lived phase that emerges from the photoexcitation process could be spin-disordered or ferromagnetic or a mixture of the two. The results of cluster calculations indicated that both are possible in the presence of unperturbed Jahn–Teller distortions [91].

The work at Diamond was extended to higher temporal resolution by operating the synchrotron in a low-$\alpha$ mode which allowed the dynamics to be studied with a resolution of approximately 10 ps [91]. However, to understand the details of photomelting antiferromagnetic
order on the femtosecond time scale requires the temporal resolution available only at an X-ray free electron laser (XFEL). The nature of the magnetic correlations during photoexcitation was therefore further studied using the XFEL at the Linac Coherent Light Source (LCLS), Stanford. RSXD at much faster time scales than possible at a synchrotron light source showed that the $(\frac{1}{4}, \frac{1}{4}, 1)$ diffraction peak wave vector changed from $l = 0.5$ to 0.47 indicating a transient incommensurate modulation of the magnetic ordering along the $c$-axis [100]. On the other hand, the in-plane lineshapes remain unchanged following photoexcitation indicating that the in-plane correlations are not affected. Furthermore, by analysing the scattering volume along $k$, for constant $l$, the decay of the excited state is found to be slower for longer length scales. The short lived incommensurate phase is speculated to arise from the effects of the hot carriers on the balance between double exchange and superexchange interactions between the Mn sites. These first results from an XFEL offer a tantalizing glimpse into the dynamics of the magnetic degrees of freedom in a highly correlated material when driven out of equilibrium.

Photoinduced melting of antiferromagnetic order in the electronic insulator NdNiO$_3$ was studied using ultrafast RSXD on the Nanoscience beamline (I06) [101]. NdNiO$_3$ exhibits a metal–insulator transition at $T \sim 150$ K at which point antiferromagnetic ordering is established. The metal-to-insulator transition is associated with charge localization onto two inequivalent Ni sites with the Ni–O bonding distance differing by approximately 4%. The resulting exchange pattern gives rise to antiferromagnetic Ni ordering in addition to a mean field ordering of the Nd sites. The energy dependence of the RSXD $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ peak over the Ni $L_3$ edge allows the

Figure 6. Time dependence of (a) the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ diffraction peak intensity recorded at $h\nu = 640.25$ eV with a laser fluence of 5.5 mJ cm$^{-2}$ and (b) the $(\frac{1}{4}, \frac{1}{4}, 0)$ diffraction peak intensity recorded at $h\nu = 641.5$ eV (filled circles) with a laser fluence of 10 mJ cm$^{-2}$. The red (grey) lines are a guide to the eye. (c) Energy dependence of the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ diffraction peak intensity before (open circles) and 200 ps after photoexcitation (filled circles). The lines represent smoothed fits to the data. (d) Energy dependence of the $(\frac{1}{4}, \frac{1}{4}, 0)$ diffraction peak intensity before (open circles) and 200 ps after photoexcitation (filled circles). The lines represent smoothed fits to the data. (Online version in colour.)
dynamics of photomelting of the antiferromagnetic order to be correlated with changes in the charge disproportionation at the Ni sites. In this study, high temporal and spectral resolution was obtained by exploiting the complementary advantages of a synchrotron radiation source and the XFEL at Stanford, USA. Figure 7a shows the time and energy dependence of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak over the Ni $L_3$ edge after ultrafast laser excitation using 800 nm laser pulses. The resonance at the Ni $L_3$ edges comprises a main peak at 851.3 eV along with a shoulder approximately 1.5 eV higher in energy. Charge transfer multiplet calculations have shown that these features are well described by a superposition of the electronic configurations $a(3d^72p^6) + b(3d^82p^5)$ with $a < b$ for one Ni site and $a > b$ for the other [102]. The relative intensities of these two features therefore yields a ratio ($\propto a/b$) that quantifies the degree of charge disproportionation and was determined using Lorentzian fits to the two peaks (figure 7b). The evolution of this ratio is shown in figure 7b with the redistribution of the spectral weight leading to a transient increase in the ratio of the peak intensities. The concomitant melting of the magnetic order is shown in figure 7c by the time-resolved decrease in the intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ diffraction peak measured at the LCLS XFEL.

These results show that ultrafast RSXD at synchrotron sources can provide new insights into the dynamics of non-equilibrium phases, and that these studies can be readily extended to the femtosecond time scale at newly available XFEL facilities. In the future, the use of femtosecond X-rays to study the microscopic texture of hidden non-equilibrium phases, by optically creating transient crystal structures with new and unexpected functionalities, may eventually allow materials to be designed with similar properties at equilibrium.
5. Nanomagnetism

(a) Domain wall motion in nanowires

Manipulating magnetic domain walls in nanostructures is currently an area of intense activity due to potential applications in spintronic devices for memory or logic. A spin-polarized current interacts with the magnetization according to a modified Landau–Lifshitz–Gilbert equation,
\[ \dot{m} = \gamma H \times m + \alpha m \times \dot{m} - (u \cdot \nabla)m + \beta (u \cdot \nabla) \times (u \cdot \nabla)m, \]
where the first two terms describe the precession and damping of a magnetic moment \( m \) in a magnetic field \( H \) with a Gilbert damping constant, \( \alpha \), and gyromagnetic ratio, \( \gamma \). The last two terms represent the adiabatic and non-adiabatic spin torque on \( m \) resulting in a domain wall velocity \( u \) \[103\]. The nature of the current-induced domain wall motion, via the spin torque, is determined by the relative size of \( \beta \) and \( \alpha \), but the ratio of these terms is not very well known for different materials. Furthermore, one of the limiting factors in depinning domain walls in a nanowire is the large current density required which results in heating and damage to the nanowire. Since the threshold current density required to depin and move a domain wall is related to the non-adiabatic part of \( \beta \) there have been several strategies developed to tune this parameter. The group of Marrows (Leeds) have used PEEM combined with XMCD on the Nanoscience beamline (I06) to study domain wall motion in magnetic nanowires with notable advances made using nanowires doped with vanadium \[104\]. By doping V into Ni$_{80}$Fe$_{20}$ nanowires the Marrows group managed to increase the spin-flip rate by introducing scattering centres for conduction electrons which in turn increased the non-adiabatic contribution to \( \beta \). The vanadium doping did not affect the value of \( \alpha \) indicating that the microscopic origins of \( \alpha \) and \( \beta \) are different. However, even though the non-adiabatic contribution to \( \beta \) was found to increase with vanadium doping, the current density required to depin a domain wall also increased due to concomitant changes in the spin-polarization and saturation magnetization of the nanowire \[104\]. The group of Kläui (Mainz) has studied domain wall motion in Ni$_{80}$Fe$_{20}$ nanowires doped with Ho (figure 8) using PEEM on beamline I06 \[105,106\]. Ho doping resulted in substantial variation in \( \alpha \) and the non-adiabatic part of \( \beta \) implying that the spin relaxation that results in the spin torque is affected by spin dissipation processes that cause viscous damping. Since V and Ho damping causes subtly different effects on the saturation magnetization, spin polarization and structural properties of the nanowires, the differences on the domain wall motion are perhaps not surprising and imply that enhancing the spin-transfer torque involves carefully tuning a complex set of interdependent properties.

The group of Marrows (Leeds) have also studied the effects of Gd doping in Ni$_{80}$Fe$_{20}$ nanowires on the depinning current densities using the Nanoscience beamline (I06). Gd doping was shown to give rise to additional spin-flip scattering leading to lower current densities required to depin and move domain walls from pinning centres \[107,108\]. In a remarkable series of experiments, Lepadatu et al. (from the Marrows group) also used Gd doping to engineer the resonant frequency required to move a domain wall around a pinning centre \[109,110\]. Since a pinning centre, such as a parabolic notch, introduces a potential well, the gradient of the total energy along the pinning centre acts as a restoring force for the domain wall. Excitation of the domain wall with an alternating current tuned to the eigenfrequency of the potential well leads to domain wall motion. The initial results demonstrated that Ni$_{80}$Fe$_{20}$ nanowires with parabolic or linear notches could be excited with resonant frequencies ranging from 10 to 50 MHz with a significant dependence on the notch profile \[110\]. However, doping the nanowires with 10% Gd resulted in an order of magnitude increase in the resonant frequency (approx. 420 MHz) arising mainly from the increased out-of-plane anisotropy allowing the magnetization to tilt out-of-plane with a reduced damping at resonance.

Domain wall imaging in novel architectures with strain, perpendicular anisotropy or antiferromagnetic components are currently active areas of study for next-generation device development. In particular, time-resolved magnetization studies using PEEM combined with XMCD at Diamond is an active area of research and should allow significant advances to be made in the ultrafast manipulation of magnetic domains.
Figure 8. PEEM images with XMCD contrast from 1500 nm wide nanowires of permalloy taken (a) before and (b) after a 25 µs current pulse which displaces the domain wall several micrometres. The inset in (a) shows a simulation of the domain wall with the arrows indicating the local direction of the magnetization. (Online version in colour.)

(b) Holographic imaging in Co/Pt/Ni$_{80}$Fe$_{20}$

PEEM is a versatile full-field imaging technique, but it is limited by aberrations introduced by the electron lenses, relies on good clean surfaces and does not work in high magnetic fields. These problems can be avoided by using high-resolution X-ray imaging techniques based on zone plates, but the ultimate resolution is then limited by the construction tolerance of the zone plate. With the advent of XFELs, there has been an increasing interest in coherent diffraction imaging which allows fast and reliable inversion of scattering patterns to generate real space images with nanometre resolution via Fourier transform holography or phase retrieval image reconstruction [111–113]. On the Nanoscience beamline (I06) Ogrin (Exeter) and co-workers have developed magnetic holography using extended reference by autocorrelation linear differential operator (HERALDO) [114]. This lensless imaging technique allows direct image reconstruction from a measurement of the Fraunhofer diffraction pattern using a sharp feature to generate the reference wave. The main advantage is that the resolution of magnetic HERALDO is not defined by the size of the reference hole, but by the quality of the sharpest feature from which the boundary waves emerge [115].

Ogrin and co-workers [116] studied Ni$_{80}$Fe$_{20}$ films grown on Co/Pt multilayers; two systems that exhibit an in-plane and out-of-plane easy axis of magnetization, respectively. Figure 9a,d shows a typical normal incidence diffraction pattern from the Co/Pt/Ni$_{80}$Fe$_{20}$ structure (shown as the difference between two holograms recorded with opposite X-ray helicities at the Co $L_3$ edge) along with the reconstructed images of the out-of-plane maze-like magnetic domains visible through the 1.5 µm aperture defining the field of view. Figure 9b,e shows a similar diffraction
Figure 9. (a) Soft X-ray hologram recorded at the Co L₃ edge with the sample surface perpendicular to the X-ray beam. (b) Hologram recorded at the Co L₃ edge with the sample surface 45° to the beam. (c) Hologram recorded at the Ni L₃ edge with the sample surface 45° to the beam. (d–f) Reconstruction of holograms shown in (a–c) revealing the domain structure in the Py layer closely matches the domain pattern in the Co/Pt layer (the blue (grey) lines in (f) show an outline of the domain pattern of the Co/Pt in (e)). The red (grey) dots in the reconstructed images indicate the same location. The orange (grey) scale bar in (f) is 500 nm. (Online version in colour.)

pattern along with the reconstructed image recorded at an angle of incidence of 45° with sensitivity to in-plane components of the magnetization. Finally, figure 9c,f shows the diffraction pattern and corresponding image recorded at the Ni L₃ edge and sensitive to the magnetic domain structure of the Ni₈₀Fe₂₀ film. The striking similarity of the magnetic domain patterns shown in figure 9e,f implies that the CoPt multilayer imprints an out-of-plane domain pattern into the Ni₈₀Fe₂₀ film. However, holograms recorded at the Ni L₃ edge and at normal incidence revealed no domain structure implying that the magnetic domains shown in figure 9f are in-plane. The origin of the Ni₈₀Fe₂₀ in-plane domain pattern is ascribed to imprinting during the growth process. The HERALDO technique therefore allows fast and element-specific imaging of magnetic domain structures, with less than 30 nm resolution and is easily extended to ultrafast time-resolved imaging of magnetic domain motion excited by strong electric or magnetic fields using, for example, an XFEL.

6. Conclusion

As we hope we have shown in this review, the contribution of the Diamond Light Source to the field of strongly correlated materials and complex magnets has clearly been remarkable in terms of both quality and breadth. Credit for this success must go to the Diamond scientists, staff and management and to the community of Diamond users who have worked extremely hard to establish Diamond as a premier institution for research in this field among a constellation of other synchrotron facilities worldwide.
Diamond users can look forward to having more tools at their disposal in the next few years: the ARPES beamline (I05) has just entered user operation and joins another leading ARPES facility (Artemis) at the Central Laser Facility on the Rutherford site [117]. A new high-resolution RIXS beamline (I21) is currently being built (with user operation expected to begin in early 2017) and is expected to further enhance the synergy between Diamond and the neutron facility (ISIS) on the Rutherford site. Meanwhile, Diamond scientists and engineers are busy planning a lattice upgrade, for the beginning of the next decade, which will result in a reduction in the horizontal emittance of the storage ring (increase in brightness) by an order of magnitude. With these developments, the future of Diamond at the leading edge of condensed matter research will be assured for decades to come.

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