Novel insight into structural magnetism by polarized synchrotron X-ray scattering

Hiroyuki Ohsumi\textsuperscript{a} and Taka-hisa Arima\textsuperscript{b,c}

\textsuperscript{a}RIKEN SPring-8 Center, Sayo, Japan; \textsuperscript{b}Department of Advanced Materials Science, University of Tokyo, Kashiwa, Japan; \textsuperscript{c}RIKEN Center for Emergent Matter Science, Wako, Japan

\textbf{ABSTRACT}

Recent increasing interest in spin-charge-entangled phenomena demands advancement of structural magnetism in order to elucidate the coupling mechanism between spin and charge of constituent electrons. This review illustrates recent developments in structural magnetism using polarized synchrotron X-ray scattering techniques, which have appropriate ability to explore hidden features in magnetic structures. The exploitation of X-ray polarization allows chiral discrimination of helimagnetic structure, evaluation of fraction of spin and orbital magnetic moments, visualization of antiferromagnetic domain distribution. The development of polarized X-ray diffractometry into microscopic observation techniques provides a scarce opportunity to investigate antiferromagnetic domain structures in detail. We present the basis of polarized X-ray diffractometry and X-ray magnetic scattering, and discuss potential directions for future developments.
1. Introduction

Magnets are ubiquitous in the modern world, being used in electric generators, motors, sensors, and magnetic media, for instance. Among a variety of magnetic materials, ferromagnetic (or ferrimagnetic) materials which possess remanent magnetization are particularly important for industrial applications and have an accumulation of dedicated techniques for magnetic domain control and observation [1–4]. On the basic science side, the significance of research on magnetic materials is, regardless of the existence of spontaneous magnetization, found in the close relationship with hot topics in modern condensed matter physics. Magnetism, one aspect of a correlated electron system [5], is a key clue to understanding fascinating phenomena such as high-$T_c$ superconductivity, spin-dependent transport, magneto-electric (ME) effect, and so on.

Arrangement of atomic magnetic moments is crucial in understanding magnetic properties of materials and is ordinarily determined by neutron diffraction experiments. The experimentally established magnetic structure exposes interatomic magnetic interactions, magnetic anisotropy, and underlying symmetry, which ensures a microscopic description of magnetic properties. A quantum state of an atomic magnetic moment is also worth identifying because the realized electron configuration is a direct consequence of intra-atomic electron correlation. X-ray magnetic circular dichroism is now well established as a technique for evaluating the respective contribution from spin and orbital motion of constitutive electrons to the atomic magnetic moment ($LS$ separation) [6,7]. However, this technique is not applicable to antiferromagnetic materials. Similarly, magnetic domain observation techniques like magnetic force microscopy [8] or magneto-optical microscopy [9] are only available for ferromagnetic (or ferrimagnetic) materials. Since there exists blanks in a lineup of experimental techniques for antiferromagamic materials, structural magnetism will be further advanced by developing missing techniques enabling $LS$ separation and magnetic domain observation.

X-ray diffraction is well established as a technique for crystal structure analysis. Although X-ray scattering occurs due to atomic magnetic moments, the observation of extremely weak magnetic reflections is quite difficult with the conventional X-ray sources [10]. The advent of synchrotron radiation sources facilitated development of X-ray magnetic diffraction techniques [11,12], and both resonant and non-resonant X-ray magnetic scattering are being exploited nowadays in structural magnetism studies. The distinctive advantages of X-ray magnetic diffraction are considered to be the ability to single out the contribution from a specific electronic state and the applicability of $LS$ separation to antiferromagnetic materials. In addition, scanning microscopy of antiferromagnetic domains is also possible with a microfocused X-ray beam. Therefore, X-ray magnetic diffraction can fill the blanks in a lineup of experimental techniques for antiferromagnetic materials and is supposed to advance structural magnetism further.
Recent increasing interest in spin-charge-entangled phenomena [13–16] has promoted antiferromagnetic materials as a potential functional material. In considering the synergy between magnetic and dielectric properties, parity-odd arrangement of magnetic moments and/or parity-odd magnetic multipole moments is important entities, and hence antiferromagnetic materials are expected to accommodate a variety of ME effects due to their rather complicated magnetic moment density distribution. As for the conventional spin orbit coupling, the latency of unprecedented phenomena is quite possible in antiferromagnetic materials due to zero ensemble average of uncontrollable multiple domains. Whereas polarized synchrotron X-ray diffraction is similar in many respects to polarized neutron diffraction, this state-of-the-art technique can realize detection of multipolar order parameters, LS separation against antiferromagnetic materials, and microscopic observation of antiferromagnetic domains. Therefore, polarized synchrotron X-ray diffraction is expected to advance structural magnetism further, which would promote structural researches on not only magnetic materials but also correlated electron systems showing fascinating phenomena.

Figure 1. (a) Schematic of polarized synchrotron X-ray scattering measurement. A linearly polarized monochromatic X-ray is delivered to the first quarter wave plate (QWP) and is converted to a circularly polarized one. The second QWP retransforms the polarization state back to a linear one being inclined depending on the rotation angle $\vartheta$ of the 2nd QWP’s principal plane about the direction of beam propagation. No use of the 2nd QWP simply provides circularly polarized X-ray to the sample. The wave vectors $k$ and $k'$ span the scattering plane and define the bases $u_i$’s as well as the direction of $\sigma$ and $\pi$. (b) The Poincaré sphere. All possible polarization states are mapped to points on the surface of the sphere. (c) Typical configurations of polarization analyzer. Polarization component along the rocking axis of an analyzer crystal is selectively reflected and reaches a detector.
The rest of this paper is organized as follows. Section 2 describes the basics of X-ray magnetic diffraction using polarized X-rays. In particular, the X-ray cross section is formalized in an ad hoc form for polarized X-ray diffractometry. The control and analysis of X-ray polarization are mentioned briefly. In Section 3, we review some typical examples of structural magnetism study on antiferromagnetic materials using polarized synchrotron X-rays. The future direction of structural magnetism using polarized synchrotron X-rays will be discussed at the end.

2. Polarized X-ray diffractometry

X-ray magnetic scattering corresponds to relativistic corrections to Thomson scattering and is thus quite small in amplitude. Another noteworthy fact about magnetic scattering is that its polarization dependence differs from that of Thomson scattering. The use of synchrotron X-rays is essential to magnetic diffraction experiments since highly brilliant X-rays produce detectable diffraction intensity and a high degree of polarization enables us to isolate magnetic scattering from omnipresent Thomson scattering. The history and fundamentals of X-ray magnetic scattering are to be found in a textbook [17] and review papers [18–20].

The X-ray cross section for elastic scattering can be written as

\[
\frac{d\sigma}{d\Omega} = r_0^2 \text{Tr} \left[ \langle M \rangle \rho_p \langle M^\dagger \rangle \right],
\]

where \( r_0 \) is the classical electron radius, \( \langle M \rangle \) and \( \langle M^\dagger \rangle \) are the interaction matrix and its Hermitian conjugate, respectively [21]. The polarization density matrix \( \rho_p \) is expressed in terms of the unit matrix \( I \), the Poincaré vector \( P \) and the Pauli matrices \( \sigma \) [22]:

\[
\rho_p = \frac{(I + P \cdot \sigma)}{2} = \left( I + P_x \sigma_x + P_y \sigma_y + P_z \sigma_z \right)/2,
\]

where \( P_x, P_y, \) and \( P_z \) are the normalized Stokes parameters. Note that the Poincaré vector \( P \) is not a vector in real space. Taking the polarization vectors \( \hat{\sigma} \) and \( \hat{\pi} \) perpendicular and parallel to the scattering plane as two orthogonal bases shown in Figure 1(a), we can write the X-ray polarization as \( \hat{\sigma} = E_\sigma \hat{\sigma} + E_\pi \hat{\pi} \) and the Pauli matrices as

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\]

The parameter \( P_z \) specifies the linear polarization perpendicular and parallel to the scattering plane; \( P_z = 1 \) \( (P_z = -1) \) corresponds to \( \hat{\sigma} \) \( (\hat{\pi}) \) polarization. The degree of circular polarization is defined by the parameter \( P_x \); \( P_x = 1 \) expresses the right-handed circular (RHC) polarization \( (i \hat{\sigma} + \hat{\pi})/\sqrt{2} \) and \( P_y = -1 \) the left-handed one \( (i \hat{\sigma} + \hat{\pi})/\sqrt{2} \).

The parameter \( P_x \) describes the linear polarization at angles \( \pm 45^\circ \) from the scattering plane; \( P_x = \pm 1 \) stands for \( (\hat{\sigma} \pm \hat{\pi})/\sqrt{2} \) polarization. The polarization state of the X-ray beam is mapped on to the so-called Poincaré sphere as shown in Figure 1(b).

Expressing the interaction matrix as follows:

\[
\langle M \rangle = M_0 I + M_x \sigma_x + M_y \sigma_y + M_z \sigma_z = M_0 I + M \cdot \sigma,
\]
the X-ray cross section for elastic scattering can be written as

\[
\frac{d\sigma}{d\Omega} = r_0^2 \left[ M_0 M_0^* + M \cdot M^* + P \cdot \left( MM_0^* + M_0 M^* - iM \times M^* \right) \right].
\] (1)

The expression includes a dot product term between the Poincaré vector \( P \) and a vector quantity \( MM_0^* + M_0 M^* - iM \times M^* \) in an abstract space. Choosing appropriate X-ray polarization \( P \) allows us to measure out each component of the vector quantity. Therefore, polarized X-ray diffractometry is advantageous especially for structural magnetism dealing with spin and orbital magnetization densities in addition to charge density, since the respective contributions can be disentangled with four different structure amplitudes determined by polarized X-ray diffractometry. Note that there is no need to exploit polarized X-ray diffractometry for studies being not interested in non Thomson scatterings.

### 2.1. Non-resonant X-ray magnetic scattering

An application of X-ray magnetic scattering to magnetic materials was first discussed by Platzman and Tzoar [23]. X-ray magnetic scattering was explored in detail by de Bergevin and Brunel [10,24,25] and Blume and Gibbs [11,21,26]. The interaction matrix of non-resonant X-ray magnetic scattering (NRXMS) can be written as \( M_{\text{NRXMS}} = -i \left( \frac{\hbar \omega}{mc^2} \right) \left[ L(K) \cdot A/2 + S(K) \cdot B \right] \), where \( K = k - k' \) is the momentum transfer, \( S(K) \) and \( L(K) \) are the Fourier transforms of spin and orbital magnetization density, respectively [21,26,27]. The matrices \( A \) and \( B \) depend on the incident (scattered) beam wavevector \( k (k') \) and the initial (final) polarization \( \hat{e} (\hat{e}') \):

\[
A = 2 \left( 1 - \hat{k} \cdot \hat{k}' \right) (\hat{e}' \times \hat{e}) - \left( \hat{k} \times \hat{e} \right) \left( \hat{k}' \cdot \hat{e}' \right) + \left( \hat{k}' \times \hat{e}' \right) \left( \hat{k} \cdot \hat{e} \right),
\]

\[
B = \hat{e}' \times \hat{e} + \left( \hat{k}' \times \hat{e}' \right) \left( \hat{k} \cdot \hat{e} \right) - \left( \hat{k} \times \hat{e} \right) \left( \hat{k}' \cdot \hat{e}' \right) - \left( \hat{k}' \times \hat{e}' \right) \times \left( \hat{k} \times \hat{e} \right).
\]

The difference between \( A \) and \( B \) enables us to separately evaluate spin and orbital magnetization densities by X-ray magnetic scattering. Note that neutron scattering does not have this ability because there is no difference between two matrices corresponding to \( A \) and \( B \). Expanding the interaction matrix for NRXMS with the Pauli matrices, we obtain

\[
M_0 = -i \sin 2\theta \frac{\hbar \omega}{mc^2} \left( u_2 \cdot S(K) + u_2 \cdot L(K) \sin^2 \theta \right),
\]

\[
M = -i \sin 2\theta \frac{\hbar \omega}{mc^2} \left( u_3 \cdot S(K) \sin \theta \tan \theta, -u_2 \cdot L(K) \sin^2 \theta \right),
\] (2)
where $2\theta$ is the scattering angle and $\mathbf{u}_i$’s the bases defined as follows (see Figure 1(a)): $\mathbf{u}_1 = \left( \hat{k} + \hat{k}' \right)/2 \cos \theta$, $\mathbf{u}_2 = \left( \hat{k} \times \hat{k}' \right)/\sin 2\theta$, $\mathbf{u}_3 = \left( \hat{k} - \hat{k}' \right)/2 \sin \theta$. It is evident that $M_0$ and $M$ depend on the orientation of a sample crystal around the scattering vector $\mathbf{K}$. This azimuthal angle dependence is also thoroughly exploited in NRXMS experiments.

2.2. Resonant X-ray magnetic scattering

The resonance enhancement of magnetic scattering amplitude was first suggested by Blume [26] and observed in pure Ni using $K$-edge by Namikawa and his collaborators [12]. The discovery of large enhancements at $L$-edges of Ho by Gibbs and his collaborators [28] stimulated subsequent theoretical and experimental works relating to resonant X-ray scattering. Following Hannon [29], resonance effects from the dominant electric dipole-electric dipole ($E1-E1$) process can be written as

$$\Delta f_{E1-E1}^{\text{RXS}} = F(0) (\hat{e}' \cdot \hat{e}) - i F(1) (\hat{e}' \times \hat{e}) \cdot \hat{m} + F(2) (\hat{e}' \cdot \hat{m})(\hat{e} \cdot \hat{m}),$$

where $\hat{m}$ is the direction of an atomic magnetic moment and the quantum mechanical factors, $F(0)$, $F(1)$ and $F(2)$. The first term has no magnetic contribution to the scattering factor but is relevant to the so-called anomalous dispersion, $f' + if''$. The third term is quadratic in $\hat{m}$ and is therefore insensitive to the sign of magnetic moments, which yields second-harmonic magnetic satellites not due to a half-pitch magnetic modulation. The second term is linear in $\hat{m}$ and gives rise to the leading term of resonant X-ray magnetic scattering (RXMS). Defining the resonant magnetic structure factor, $F_m(K) = \sum_n e^{iK \cdot r_n} F_n^{(1)} \hat{m}$, the interaction matrix of RXMS is written as $\left< M_{\text{RXMS}} \right> = -i (\hat{e}' \times \hat{e}) \cdot F_m(K)$. Following Hill and McMorrow [30], we obtain

$$M_0 = i u_2 \cdot F_m(K) \sin \theta \cos \theta,$$
$$M = \left( -i u_3 \cdot F_m(K) \sin \theta, \ u_1 \cdot F_m(K) \cos \theta, -i u_2 \cdot F_m(K) \sin \theta \cos \theta \right).$$

The interaction matrix of RXMS alters when higher order transition processes are not negligible. Taking electric quadrupole $E2$ transition into account and neglecting magnetic $M1$ transition leads to the resonant scattering cross section related to electromagnetic multipoles [31], which is also known as anisotropy of the tensor of susceptibility (ATS) scattering [32,33].

2.3. Control and analysis of X-ray polarization

Dynamical theory of X-ray diffraction [34] leads to unequal dispersion relation between $\sigma$ and $\pi$ polarization inside a perfect crystal near the Laue-Bragg
condition. Exploiting this diffractive birefringence, one can attain phase retardation between both polarization components of transmitted beam and configure an X-ray phase retarder [35–37]. The phase retardation depends on the deviation \( \Delta \theta \) from the exact Bragg angle, and hence polarization of the transmitted beam can be controlled by adjusting \( \Delta \theta \). Generally, the scattering plane of an X-ray phase plate is set to be inclined at 45° from the horizontal plane since synchrotron radiation is linearly polarized in the horizontal plane. With a quarter-wave plate (QWP) configuration, the linearly polarized incident X-ray is converted to a circularly polarized X-ray. Circular polarization is essential for identification of vector spin chirality [38–41] and detection of interference effects between charge and magnetic scattering [42,43]. Installing another QWP downward and rotating its principal plane about the direction of beam propagation, the circular polarization is reconverted to arbitrary inclined linear polarization as shown in Figure 1(a). The polarized X-ray diffractometry using the inclined linear polarizations considerably facilitates not only \( LS \) separation [44,45] but also disentanglement of close-lying dipole and quadrupole resonances [46,47], which improve the feasibility of X-ray magnetic structure determination. It is possible to rotate X-ray polarization using another type of double-phase-plate system [48,49].

Thomson scattering at a right angle results in thorough suppression of \( \pi \)-polarized X-rays. Linear polarization analysis of X-rays is carried out exploiting this phenomenon and offers a straightforward decomposition into \( \sigma \) and \( \pi \) components as shown in Figure 1(c). However, a perfect linear-polarization analysis is only possible when \( 2\theta = 90^\circ \), and therefore the X-ray energy is restricted to certain values determined from an employed analyzer crystal. For RXMS experiments, decomposition of X-ray polarization becomes imperfect as the scattering angle deviates from exact right angles, which requires elaborate analyses in order to disentangle the contributions from \( \sigma \) and \( \pi \) polarizations. The interaction matrix for Thomson scattering is written as \( \langle M_{\text{Thomson}} \rangle = \rho(K)(\hat{e}' \cdot \hat{e}) \), where \( \rho(K) \) is the Fourier transforms of the electronic charge density of the analyzer crystal. The rotation of the analyzer crystal by \( \chi_A \) about the direction of incidence is taken into account as follows: \( \langle M_{\text{Analyzer}} \rangle = \rho(K)(\hat{e}' \cdot \hat{e}) \left[ \cos \chi_A I + i \sin \chi_A \sigma_y \right] \). Then, the explicit expression of the cross section for the rotated analyzer crystal becomes \( d\sigma/d\Omega = r_0^2|\rho(K)|^2 \left[ 1 - 2 \sin^2 \theta \cos^2 \theta + 2 \sin^2 \theta \cos^2 \theta \left( P_x \sin 2\chi_A + P_z \cos 2\chi_A \right) \right] \). One can evaluate the degrees of linear polarization \( P_x \) and \( P_z \) by analyzing the \( \chi_A \) dependence of X-ray intensity passing through the polarization analyzer with this expression. However, the use of a crystal analyzer decreases the observed intensities due to quite low X-ray reflectivity around \( 2\theta = 90^\circ \).

3. **Novel developments in structural magnetism**

The first magnetic structure determination was accomplished using neutron diffraction by Shull and Smart in 1949 [50]. Thereafter, neutron diffraction has remained the most powerful experimental technique for magnetic structure
analysis and has uncovered numerous magnetic structures. However, the complementary use of synchrotron X-ray diffraction is nowadays worth considering in some cases: neutron absorbing compounds, element specific investigation, $LS$ separation, and high $q$-resolution measurement. In addition, X-ray magnetic diffraction techniques also leave scope for advancement. Therefore, new development of structural magnetism is highly expected to take place by fully exploiting these unconventional techniques. We will show below several distinctive embodiments of structural magnetism by polarized synchrotron X-ray scattering.

3.1. Spin-driven ferroelectricity

Two fundamental physical properties, magnetism and dielectricity, are highly independent of each other due to their difference in time–space symmetry: magnetization is odd under time reversal and even under space inversion, and electric polarization vice versa. The creation of magnetoelectrically coupled materials is therefore a formidable challenge but is a worthwhile effort toward development of a new class of materials possessing synergetic functions of magnetic and electric properties. The concept of ME effects was first proposed by Curie in the late nineteenth century [51]. After several decades of silence, ME effects in $\text{Cr}_2\text{O}_3$ were theoretically predicted by Dzyaloshinskii [52], which was subsequently confirmed by experiments [53,54]. However, the tiny ME effects had not encouraged further applied researches until recently. The discovery of gigantic ME effects in $\text{TbMnO}_3$ [55] has revived research interests toward the development of magnetoelectrically coupled materials, which led to the substantial progress in the area of multiferroics [13–15].

Spontaneous electric polarization of $\text{TbMnO}_3$ exhibits strong dependence on applied magnetic fields [55]. The underlying magnetic structure was promptly ascertained to be a cycloid magnetic structure lacking inversion symmetry [56,57] and was in good accordance with the theoretical prediction [58]. The magnetoelectrically induced electric polarization $\vec{P}_{ij}$ is given by $\vec{P}_{ij} \propto \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$ where $\vec{e}_{ij}$ is the vector connecting atomic sites of $\vec{S}_i$ and $\vec{S}_j$ [58]; the vector spin chirality $\vec{S}_i \times \vec{S}_j$ between two adjacent magnetic moments has a non-zero value and is uniform within a monodomain cycloid. The application of magnetic fields induces changes in electric polarization through a modification in spin arrangement as a consequence of the ME coupling mentioned above. The question then arose whether external electric fields influence the cycloid magnetic structure. Polarized neutron diffraction on $\text{TbMnO}_3$ [59] first confirmed that the sense of vector spin chirality can be controlled by electric-field cooling procedure. The subsequent NRXMS study succeeded in providing more detailed information about the magnetic structure of $\text{TbMnO}_3$ [40], although detailed analysis required measurements at extremely low-count rates. The establishment of cycloidal spin arrangement in ferroelectric phase of $\text{DyMnO}_3$ was confirmed using NRXMS owing to quite
large neutron absorption of dysprosium [41]. Using submillimeter X-ray beam, helimagnetic domain imaging was attempted on multiferroic Ni$_3$V$_2$O$_8$ [60] and BiFeO$_3$ [61].

Circularly polarized X-rays have the ability to distinguish helicity of spiral antiferromagnets [38]. We show here the simple example of this type of experiment. MnWO$_4$, a prototypical multiferroic material [62,63], has a monoclinic crystal structure of a space group $P2_1/c$. In the ferroelectric phase ($7.6 < T < 12.7$ K), Mn$^{2+}$ spins on 2$f$ site form a spiral with a propagation vector $q = (-0.214, 1/2, 0.457)$; the spin $S_{l,m}$ on the $m$-th Mn$^{2+}$ ion in the $l$-th cell is written as

$$S_{l,m} = S_{\text{easy}} \cos \left(2\pi q \cdot r_l + \phi_m\right) \pm S_b \sin \left(2\pi q \cdot r_l + \phi_m\right), \quad (4)$$

where $S_b$ and $S_{\text{easy}}$ are the directional components along the $b$-axis and the easy axis being at an angle of 34° from the $a$-axis toward the $c$-axis. The electric polarization is induced along the $b$-axis being perpendicular to both the cross product $S_{\text{easy}} \times S_b$ and the spin chain along the $c$-axis. The (012)-plate sample was cooled in $b$-axis poling electric fields of ±80 kV/m across the transition temperature of 12.7 K, and scan profiles of the magnetic satellite $\bar{0}12 + q$ were measured using circularly polarized X-rays of 8.40 keV. The satellite reflection becomes distinct with $P_b > 0$ for RHC polarization and $P_b < 0$ for left-handed circular (LHC) polarization, as shown in Figure 2(a). The interaction matrix for this reflection is written as

$$M_0 = i \sin 2\theta \frac{h\omega}{mc^2} A \left( S_{\text{easy}} \cos \alpha \sin \beta \mp i S_b \cos \beta \right),$$

$$M = i \sin 2\theta \frac{h\omega}{mc^2} A \left( \left( S_{\text{easy}} \cos \alpha \cos \beta \pm i S_b \sin \beta \right) \sin \theta \tan \theta, -S_{\text{easy}} \sin \alpha \sin \theta, 0 \right),$$

where [012] is parallel to $u_1$, $\alpha$ the angle between the easy axis and the surface normal, $\beta$ the angle between the scattering vector and the surface normal, and $A = i^d e^{-id\phi_b} \cos (0.471\pi)$. As the ellipticity of helix $m_b/m_{\text{easy}}$ at 8.5 K is almost equal to one [64,65], the cross section is represented as follows: $d\sigma/d\Omega = \left(0.001 r_0 S\right)^2 \left[1.420 + P \cdot (-0.070, \pm 1.000, 0.001)\right]$, where the double sign coincides with that in Equation (4). The plus sign corresponds to a right-handed spin helix and leads to comparative advantage of RHC in reflection intensity, and the minus sign vice versa. Consequently, as shown in Figure 2(b), the positively ($P_b > 0$) and negatively ($P_b < 0$) polarized domains possess the right- and left-handed helical spin structures, respectively. The result clearly demonstrates the spin-driven ferroelectricity, the ME coupling effect induced by magnetic structures violating space inversion symmetry. ME multiferroics are a new direction of potential applications of antiferromagnetic materials. Approaches based on structural magnetism are well suited for ME multiferroics and indeed played an important role in confirming the relation between vector spin chirality and electric polarization.
3.2. Spin-orbit Mott insulator

The spin and orbital motion of electrons give rise to a magnetic moment. In condensed matter, outer-shell electrons are exposed to the crystal electric field of surrounding ions and tend to occupy orbitals described with cubic harmonics rather than spherical harmonics, resulting in quenching of the orbital angular momentum as seen in $3d$ transition metal oxides. On the other hand, an ineffective crystal electric field leaves spherical orbitals degenerate, and the unquenched orbital angular momentum couples with spin angular momentum through the spin-orbit interaction. In investigations of magnetic anisotropy, the evaluation of constituent orbital angular momentum is required despite being no longer a good quantum number. In addition, recent rising interest in heavier transition metal oxides makes it more important to identify spin and orbital states in detail for a better understanding of unconventional electronic phases.

$5d$ transition metal oxide $\text{Sr}_2\text{IrO}_4$ is a magnetic insulator [66], contrary to the expectation that it should have a metallic ground state due to relatively wide band width and weak Coulomb interactions compare to $3d$ transition metals. Recently, RMXS has uncovered the unconventional Mott insulating state...
induced by the strong spin-orbit coupling inherent to 5\textit{d} transition metals [67], where a half-filled band of an effective total angular momentum \( J_{\text{eff}} = 1/2 \) state is separated by a charge gap as a consequence of electron correlation [68]. The selection rule of RMXS, forbidden at the Ir \( L_{\text{II}} \) edge, indicated the realization of the \( J_{\text{eff}} = 1/2 \) state in Sr\(_2\)IrO\(_4\) and other iridium oxides [69–72]. However, it is unrealistic not to consider deviations from the ideal \( J_{\text{eff}} = 1/2 \) state expressed as

\[
\sigma = \frac{1}{\sqrt{3}} \left( \pm \frac{1}{2}, \pm \frac{1}{2} \right) \pm \frac{1}{\sqrt{3}} \left( \pm \frac{1}{2}, \pm \frac{1}{2} \right) + i \frac{1}{\sqrt{3}} \left( \pm \frac{1}{2}, \pm \frac{1}{2} \right)
\]

where \( m \) is the magnetic quantum number of \( J_{\text{eff}} \) and \( \sigma \) the spin state, and therefore the LS separation technique is greatly anticipated to manifest its ability.

Details of the constituent spin and orbital magnetic moments can be clarified from the dependence of magnetic scattering intensity on an inclination angle of linear polarization [44]. A layered perovskite Sr\(_2\)IrO\(_4\), a prototypical spin-orbit Mott insulator [67], has a tetragonal crystal structure of a space group \( I4_{1}/acd \). Below the Néel temperature around 240 K, atomic magnetic moments of Ir\(^{4+}\) ions on 8\textit{a} site form a canted antiferromagnetic structure as shown in Figure 3. The major \( b \)-axis component consists of an antiferromagnetic stacking of the ferromagnetic \( ac \)-plane and the minor \( a \)-axis component has the up–down–down–up stacking sequence of the ferromagnetic \( ab \)-plane. The (001)-plate sample was cooled down to 10 K, and rocking curves of the magnetic reflection 1 0 22 were measured with linearly polarized X-rays of 10.45 keV. Figure 4 shows the inclination angle \( \vartheta_{\text{pol}} \) dependence of charge and magnetic scattering, which are the background level of a rocking curve and the integrated intensity of the magnetic reflection. The interaction matrix for this reflection in the \( b||u_2 \) geometry is written as

\[
M_0 = i \sin 2\vartheta \frac{h_0}{mc} (-S - L \sin^2 \theta), \quad M = i \sin 2\vartheta \frac{h_0}{mc} (0, 0, L \sin^2 \theta).
\]

\textbf{Figure 3.} (Left) crystal and (right) magnetic structures of Sr\(_2\)IrO\(_4\). Notes: Yellow, orange, and green spheres represent Ir, O, and Sr atoms, respectively. On the right panel, ordering pattern of \( J_{\text{eff}} = 1/2 \) moments in each IrO\(_2\) layer is depicted on plan view drawings.
Then, the cross section is represented as
\[
\frac{d\sigma}{d\Omega} = (0.018r_0S)^2 \left[ 1 + 0.534\eta + 0.142\eta^2 - P \cdot (0, 0, 0.534\eta + 0.142\eta^2) \right]
\]
where \(\eta = L/S\) and \(P = \left( P \sin 2\theta_{pol}, 0, P \cos 2\theta_{pol} \right)\). The degree of linear polarization \(P\) was evaluated for this setup as 0.984 [73]. Thomson scattering at \(2\theta = 62.2^\circ\) explains the polarization dependence of charge scattering, and that of magnetic scattering is well reproduced with \(\eta = 5.0 \pm 0.7\), which is much larger than the expectation value for the ideal \(J_{\text{eff}} = 1/2\) state (\(\eta = 3.5\)) [45]. The observed enhancement in
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Orbital contribution cannot be attributed to a rebalance within $5d-t_{2g}$ but requires hybridization with other orbital states to be taken into account. The spin-orbit Mott insulator is a new type of correlated electron system and quite different from the conventional Mott insulator. Note that the use of polarized X-ray diffractometry was essential in establishing the concept of the spin-orbit Mott insulator [45], because the conventional $L_S$ separation technique [28,74,75] must need unfeasible measuring time to compensate for the low efficiency of a polarization analyzer.

3.3. All-in-all-out (AIAO) type antiferromagnet

Direct access to antiferromagnetic order parameters is hardly attained other than diffractometry, since the antiferromagnetic order parameters are macroscopically invisible due to zero net magnetic moment. The same difficulty arises in the observation of magnetic domains, and therefore the conventional observation techniques for ferromagnetic domains are not applicable to antiferromagnetic domains. Magnetic diffraction using a microfocused X-ray beam is a straightforward approach to visualize antiferromagnetic domains. Such scanning X-ray microscopy experiments indeed succeeded in imaging magnetic domains of Cr [76], Ho [39], Ni$_3$V$_2$O$_8$ [60], BiFeO$_3$ [61], Cd$_2$Os$_2$O$_7$ [43]. Details of the magnetic X-ray microdiffraction techniques are to be found in a review paper [19].

5$d$ pyrochlore oxide Cd$_2$Os$_2$O$_7$ exhibits a metal-insulator transition accompanying a magnetic anomaly [77]. Relatively high Néel temperature of 227 K conflicts with a geometrically frustrated Os$^{5+}$ pyrochlore lattice. The establishment of an all-in-all-out (AIAO) type magnetic order (see Figure 5) was ascertained.

Figure 6. 0 0 10 Forbidden reflection dark field images of the Cd$_2$Os$_2$O$_7$ crystal at 100 K. Notes: (a) A crystal shape outlined onto the raster image of magnetic domains. All-in-all-out (AIAO) and all-out-all-in (AOAl) configurations are differentiated from each other in terms of their sign of the flipping ratio. (b), (c) Flipping ratio chart, magnetic domain distribution, on the (1T1) and (1T1) facets, respectively. (d), (e) intensity contour on the (1T1) and (1T1) facets, respectively. The intensity is normalized to the mean value on each facet. All scale bars are 100 μm across. Excerpt from Ref. [43].
by NMR and RXMS experiments [78]. The identical magnetic order is also seen in the insulating phase of pyrochlore iridates [79,80], in which unprecedented electronic phases like the Weyl semimetal [81] are anticipated to appear. In addition, unconventional linear responses to a magnetic field are predicted in the magnetostriction, magnetocapacitance, Voigt magnetooptic effect, and magnetic susceptibility [82]. There are two interrelating configurations under time reversal symmetry operation: the pyrochlore lattice is a three-dimensional network of corner sharing regular tetrahedra; the four magnetic moments on the corners of every tetrahedron all point their center (all-in) or the opposite direction (all-out); the alternate network of the two types of tetrahedra results in a zinc blende structure; the noncentrosymmetric arrangement of magnetic moments has two variants and may lead to the unconventional linear responses to a magnetic field. Magnetic domain walls also attract high attention as a possible interface possessing unconventional magnetotransport properties.

Polarized X-rays can provide a contrast between the AIAO and the all-out-all-in (AOAI) configurations. Cd$_2$Os$_2$O$_7$ has a cubic crystal structure of a space group $Fd\bar{3}m$, which gives rise to the $00l$ ($l = 4n + 2$) and the $0kl$ ($k + l = 4n + 2$) forbidden reflections. Tuning X-ray energy to the Os $L_{III}$ edge induces a resonant enhancement of the atomic scattering factor, and then, the forbidden reflections gain some intensity due to ATS scattering [32,33]. Below the Néel temperature, resonant magnetic scattering rises up over the ATS scattering. The interaction matrix for the forbidden reflection is written as

$$M_0 = F_{ATS}(1 + \sin^2 \theta), \quad M = (\mp 2iF_m \sin \theta, 0, F_{ATS} \cos^2 \theta)$$

where $[1 1 0]$ is parallel to $u_2$, $F_{ATS}$ is the amplitude of ATS, and $F_m$ the amplitude of RXMS. Then, the cross section becomes as follows:

$$\frac{d\sigma}{d\Omega} = 2r_0^2 |F_{ATS}|^2 (1 + \sin^4 \theta) + |F_m|^2 (2 \sin^2 \theta)$$

$$+ P \cdot \left( \pm \text{Im} [F_{ATS}^* F_m] 2 \sin \theta (1 + \sin^2 \theta), \quad \pm \text{Re} [F_{ATS}^* F_m] 2 \sin \theta \cos^2 \theta, \quad |F_{ATS}|^2 (1 + \sin^2 \theta) \cos^2 \theta \right),$$

where the double sign +/- stands for AIAO/AOAI configurations, respectively. Note that interference between RXMS and ATS gives rise to a contrast depending on the configurations. Figure 6 shows the $00l$ ($l = 10$) forbidden reflection dark field image of the as-grown Cd$_2$Os$_2$O$_7$ crystal at 100 K [43]. The raster scan images were acquired using a circularly polarized X-ray microbeam with a probe size of 500 × 500 nm$^2$. Antiferromagnetic domain distribution on the $(0 0 1)$ and the adjacent $(1 1 1)$ facets is clearly visualized on charts of flipping ratio $R = (I_R - I_L)/(I_R + I_L)$, where $I_R$ and $I_L$ are the reflection intensities measured with RHC and LHC polarizations, respectively (see Figure 6(a)). For the $00l$ ($l = 10$) forbidden reflection, the flipping ratio is explicitly given by

$$R = \pm \text{Re} [F_{ATS}^* F_m] \sqrt{\left( 1.430 |F_{ATS}|^2 + 0.820 |F_m|^2 \right)},$$

where the double sign again corresponds to the respective configurations. The domain walls exhibit some explicit preferential orientations as shown in Figure 6(b) and (c), which strongly indicates that the magnetic domain walls are parallel to the $(1 1 0)$ planes. This type of magnetic domain wall is very plausible because $(1 1 0)$ mirror planes interconvert AIAO and AOAI configurations. In
other words, \{1 1 0\} magnetic domain walls are consistent with the irreducible representation of the magnetic structure. Figure 6(d) and (e) show intensity contour on each facet, which visualize inhomogeneity in a crystal structure. It is clearly seen that crystal defects accompany magnetic domain walls but some magnetic domain walls are independent of crystal defects. As demonstrated here, visualization of domain structures can contribute new insight for domain engineering. Antiferromagnetic domain imaging can also expose broken symmetries owing to the occurrence of magnetic order, which are definite information for representation analysis of a magnetic structure. As demonstrated above, the development of microscopic observation techniques promotes new approaches and will advance structural magnetism further.

4. Conclusion

This review illustrates novel developments in structural magnetism exploiting polarized synchrotron X-ray scattering techniques. It is shown that polarized X-ray diffractometry has the appropriate ability to expose hidden features in magnetic structures through the investigations on spin-driven ferroelectrics, spin-orbit Mott insulator and AIAO type antiferromagnet. Its potential as a microscopic observation technique is also demonstrated in imaging antiferromagnetic domains. The potential of polarized synchrotron X-ray scattering is also recognized in other research field such as multipole-related phenomena. Even though further possibilities would be there, the use of synchrotron X-rays is worth considering in following cases: element specific investigation, LS separation, high \(q\)-resolution measurement, microscopic observation, and neutron absorbing compounds.

In particular, polarized X-ray diffraction microscopy is a promising direction of development and will provide important magnetic structural information being difficult to obtain by other techniques. The development into time-resolved experiments is also a promising direction to study the real-time evolution of magnetic structure. Upgrading of synchrotron radiation sources will bring about necessary increase in X-ray brilliance for these types of photon-consuming experiments. Spatially and temporally resolved observation of magnetic structures will ensure the microscopic understanding of spin-charge-entangled phenomena and will open up a new horizon for structural materials science research on emergent phenomena.

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Disclosure statement

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References

[1] C. Chappert, A. Fert and F.N. Van Dau, Nat. Mater. 6 (2007) pp.813–823.
[2] A.V. Kimel, A. Kirilyuk and T. Rasing, Laser & Photon. Rev. 1 (2007) pp.275–287.
[3] Y.-H. Chu, L.W. Martin, M.B. Holcomb, M. Gajek, S.-J. Han, Q. He, N. Balke, C.-H. Yang, D. Lee, W. Hu, Q. Zhan, P.-L. Yang, A. Fraile-Rodriguez, A. Scholl, S.X. Wang and R. Ramesh, Nat. Mater. 7 (2008) pp.478–482.
[4] M.R. Freeman and B.C. Choi, Science 294 (2001) pp.1484–1488.
[5] M. Imada, A. Fujimori and Y. Tokura, Rev. Mod. Phys. 70 (1988) pp.1039–1263.
[6] B.T. Thole, P. Carra, F. Sette and G. van der Laan, Phys. Rev. Lett. 68 (1992) pp.1943–1946.
[7] P. Carra, B.T. Thole, M. Altarelli and X. Wang, Phys. Rev. Lett. 70 (1993) pp.694–697.
[8] D. Rugar, H.J. Mamin, P. Guethner, S.E. Lambert, J.E. Stern, I. McFadyen and T. Yogi, J. Appl. Phys. 68 (1990) pp.1169–1183.
[9] J. McCord, J. Phys. D: Appl. Phys. 48 (2015) pp.333001–333043.
[10] F. de Bergevin and M. Brunel, Phys. Lett. A. 39 (1972) pp.141–142.
[11] D. Gibbs, D.E. Moncton, K.L. D’Amico, J. Bohr and B. Grier, Phys. Rev. Lett. 55 (1985) pp.234–237.
[12] K. Namikawa, M. Ando, T. Nakajima and H. Kawata, J. Phys. Soc. Jpn. 54 (1985) pp.4099–4102.
[13] W. Eerenstein, N.D. Mathur and J.F. Scott, Nature 442 (2006) pp.759–765.
[14] Y. Tokura, Science 312 (2006) pp.1481–1482.
[15] Y. Tokura, J. Magn. Magn. Mater. 310 (2007) pp.1145–1150.
[16] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnar, M.L. Roukes, A.Y. Chtchelkanova and D.M. Treger, Science 294 (2001) pp.1488–1495.
[17] S.W. Lovesey and S.P. Collins, X-ray Scattering and Absorption by Magnetic Materials, Clarendon Press, Oxford, 1996.
[18] W.G. Stirling and M.J. Cooper, J. Magn. Magn. Mater. 200 (1999) pp.755–773.
[19] P.G. Evans and E.D. Isaacs, J. Phys. D: Appl. Phys. 39 (2006) pp.R245–R263.
[20] M. Blume, J. Phys. Soc. Jpn. 75 (2006) p.111005.
[21] M. Blume and Donn Gibbs, Phys. Rev. B 37 (1988) pp.1779–1789.
[22] U. Fano, Rev. Mod. Phys. 29 (1957) pp.74–93.
[23] P.M. Platzman and N. Tzoar, Phys. Rev. B 2 (1970) pp.3556–3559.
[24] F. de Bergevin and M. Brunel, Acta. Cryst. A 37 (1981) pp.314–324.
[25] M. Brunel and F. de Bergevin, Acta. Cryst. A 37 (1981) pp.324–331.
[26] M. Blume, J. Appl. Phys. 57 (1985) pp.3615–3618.
[27] G.T. Trammell, Phys. Rev. 92 (1953) p.1387.
[28] D. Gibbs, D.R. Harshman, E.D. Isaacs, D.B. McWhan, D. Mills and C. Vettier, Phys. Rev. Lett. 61 (1988) pp.1241–1244.
[29] J.P. Hannon, G.T. Trammell, M. Blume and D. Gibbs, Phys. Rev. Lett. 61 (1988) pp.1245–1248.
[30] J.P. Hill and D.F. McMorrow, Acta Cryst. Sect. A 52 (1996) pp.236–244.
[31] S. Di Matteo, J. Phys. Conf. Ser. 211 (2010) p.012008.
[32] D.H. Templeton and L.K. Templeton, Acta Cryst. Sect. A 36 (1980) pp.237–241.
[33] V.E. Dmitrienko, Acta Cryst. Sect. A 39 (1983) pp.29–35.
[34] B.W. Batterman and H. Cole, Rev. Mod. Phys. 36 (1964) pp.681–717.
[35] K. Hirano, K. Izumi, T. Ishikawa, S. Annaka and S. Kikuta, Jpn. J. Appl. Phys. 30 (1991) pp.L407–L410.
[36] J.A. Golovchenko, B.M. Kincaid, R.A. Levesque, A.E. Meixner and D.R. Kaplan, Phys. Rev. Lett. 57 (1986) pp.202–205.
[37] K. Hirano, T. Ishikawa and S. Kikuta, Rev. Sci. Instrum. 66 (1995) pp.1604–1609.
[38] C. Sutter, G. Grübel, C. Vettier, F. de Bergevin, A. Stunault, D. Gibbs and C. Giles, Phys. Rev. B 55 (1987) pp.954–959.
[39] J.C. Lang, D.R. Lee, D. Haskel and G. Srajer, J. Appl. Phys. 95 (2004) pp.6537–6539.
[40] F. Fabrizi, H.C. Walker, L. Paolasini, F. de Bergevin, A.T. Boothroyd, D. Prabhakaran and D.F. McMorrow, Phys. Rev. Lett. 102 (2009) p.237205.
[41] H. Sagayama, N. Abe, K. Taniguchi, T. Arima, Y. Yamasaki, D. Okuyama, Y. Tokura, S. Sakai, T. Morita, T. Komesu, H. Ohsumi and M. Takata, J. Phys. Soc. Jpn. 79 (2010) pp.043711.
[42] J. Pollmann, G. Srajer, J. Maser, J.C. Lang, C.S. Nelson, C.T. Venkataraman and E.D. Isaacs, Rev. Sci. Instrum. 71 (2000) pp.2386–2390.
[43] S. Tardif, S. Takeda, H. Ohsumi, J. Yamaura, D. Okuyama, Z. Hiroi, M. Takata and T. Arima, Phys. Rev. Lett. 114 (2015) p.147205.
[44] H. Ohsumi, M. Mizumaki, S. Kimura, M. Takata and H. Suematsu, Physica B 345 (2004) pp.258–261.
[45] S. Fujiyama, H. Ohsumi, K. Ohashi, D. Hirai, B.J. Kim, T. Arima, M. Takata and H. Takagi, Phys. Rev. Lett. 112 (2014) p.016405.
[46] C. Mazzoli, S.B. Wilkins, S. Di Matteo, B. Detlefs, C. Detlefs, V. Scagnoli, L. Paolasini and P. Ghigna, Phys. Rev. B 76 (2007) p.195118.
[47] R.D. Johnson, S.R. Bland, C. Mazzoli, T.A.W. Beale, C.-H. Du, C. Detlefs, S.B. Wilkins and P.D. Hatton, Phys. Rev. B 78 (2008) p.104407.
[48] V. Scagnoli, C. Mazzoli, C. Detlefs, P. Bernard, A. Fondacaro, L. Paolasini, F. Fabrizi and F. de Bergevin, J. Synchrotron Rad. 16 (2009) pp.778–787.
[49] K. Okitsu, Y. Ueji, K. Sato and Y. Amemiya, J. Synchrotron Rad. 8 (2001) pp.33–37.
[50] C.G. Shull and J.S. Smart, Phys. Rev. 76 (1949) pp.1256–1257.
[51] P. Curie, J. Phys. Theor. Appl. 3 (1894) pp.393–415.
[52] I.E. Dzyaloshinskii, Sov. Phys. JETP 10 (1960) pp.628–629.
[53] D.N. Astrov, Sov. Phys. JTEP 13 (1961) pp.729–733.
[54] G.T. Rado and V.J. Folen, Phys. Rev. Lett. 7 (1961) pp.310–311.
[55] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, Nature 426 (2003) pp.55–58.
[56] M. Kenzelmann, A.B. Harris, S. Jonas, C. Broholm, J. Schefer, S.B. Kim, C.L. Zhang, S.-W. Cheong, O.P. Vajk and J.W. Lynn, Phys. Rev. Lett. 95 (2005) p.087206.
[57] T. Arima, A. Tokunaga, T. Goto, H. Kimura, Y. Noda and Y. Tokura, Phys. Rev. Lett. 96 (2006) p.097202.
[58] H. Katsura, N. Nagaosa and A. Balatsky, Phys. Rev. Lett. 95 (2005) p.057205.
[59] Y. Yamasaki, H. Sagayama, T. Goto, M. Matsuura, K. Hirota, T. Arima and Y. Tokura, Phys. Rev. Lett. 98 (2007) p.147204.
[60] F. Fabrizi, H.C. Walker, L. Paolasini, F. de Bergevin, T. Fennell, N. Rogado, R.J. Cava, Th Wolf, M. Kenzelmann and D.F. McMorrow, Phys. Rev. B 82 (2010) p.024434.
[61] R.D. Johnson, P. Barone, A. Bombardi, R.J. Bean, S. Picozzi, P.G. Radaelli, Y.S. Oh, S.-W. Cheong and L.C. Chapon, Phys. Rev. Lett. 110 (2013) p.217206.
[62] K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa and T. Arima, Phys. Rev. Lett. 97 (2006) p.097203.
[63] A.H. Arkenbout, T.T.M. Palstra, T. Siegrist and T. Kimura, Phys. Rev. B 74 (2006) p.184431.
[64] G. Lautenschläger, H. Weitzel, T. Vogt, R. Hock, A. Böhlm, M. Bonnet and H. Fuess, Phys. Rev. B 48 (1993) p.6087.
[65] H. Sagayama, K. Taniguchi, N. Abe, T. Arima, M. Soda, M. Matsuura and K. Hirota, Phys. Rev. B 77 (2008) p.220407(R).
[66] G. Cao, J. Bolivar, S. McCall, J.E. Crow and R.P. Guertin, Phys. Rev. B 57 (1998) p.R11039 (R).
[67] B.J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi and T. Arima, Science 323 (2009) pp.1329–1332.
[68] B.J. Kim, H. Jin, S.J. Moon, J.-Y. Kim, B.-G. Park, C.S. Leem, J. Yu, T.W. Noh, C. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao and E. Rotenberg, Phys. Rev. Lett. 101 (2008) p.076402.
[69] J.W. Kim, Y. Choi, J. Kim, J.F. Mitchell, G. Jackeli, M. Daghofer, J. van den Brink, G. Khaliullin and B.J. Kim, Phys. Rev. Lett. 109 (2012) p.037204.
[70] S. Boseggia, R. Springell, H.C. Walker, H.M. Ronnow, Ch Rüegg, H. Okabe, M. Isobe, R.S. Perry, S.P. Collins and D.F. McMorrow, Phys. Rev. Lett. 110 (2013) p.117207.
[71] S. Fujiyama, K. Ohashi, H. Ohsumi, K. Sugimoto, T. Takayama, T. Komesu, M. Takata, T. Arima and H. Takagi, Phys. Rev. B 86 (2012) p.174414.
[72] S. Boseggia, R. Springell, H.C. Walker, A.T. Boothroyd, D. Prabhakaran, D. Wermeille, L. Boucheneire, S.P. Collins and D.F. McMorrow, Phys. Rev. B 85 (2012) p.184432.
[73] Rocking curves of the analyzer crystal [graphite (0 0 8)] were recorded at every 20 degrees of the angle $\chi_A$. Integrated intensities were fitted with the expression given in Section 2.3, yielding the Stokes parameters. Polarization analysis was carried out every 15 degrees of the inclination angle $\vartheta_{pol}$. The degree of linear polarization, root mean square of $P_x$ and $P_z$, was determined by averaging the experimentally evaluated values for various $\vartheta_{pol}$.
[74] R. Caciuffo, L. Paolasini, A. Sollier, P. Ghigna, E. Pavarini, J. van den Brink and M. Altarelli, Phys. Rev. B 65 (2002) p.174425.
[75] S. Langridge, G.H. Lander, N. Bernhoeft, A. Stunault, C. Vettier, G. Grübel, C. Sutter, F. de Bergevin, W.J. Nuttall, W.G. Stirling, K. Mattenberger and O. Vogt, Phys. Rev. B 55 (1997) pp.6392–6398.
[76] P.G. Evans, E.D. Isaacs, G. Aeppli, Z. Cai and B. Lai, Science 295 (2002) pp.1042–1045.
[77] A.W. Sleight, J.L. Gillson, J.F. Weiher and W. Bindloss, Solid State Commun. 14 (1974) pp.357–359.
[78] J. Yamaura, K. Ohgushi, H. Ohsumi, T. Hasegawa, I. Yamauchi, K. Sugimoto, S. Takeshita, A. Tokuda, M. Takata, M. Udagawa, M. Takigawa, H. Harima, T. Arima and Z. Hiroi, Phys. Rev. Lett. 108 (2012) p.247205.
[79] K. Tomiyasu, K. Matsuhiro, K. Iwasawa, M. Watahiki, S. Takagi, M. Wakeshima, Y. Hinatsu, M. Yokoyama, K. Ohoyama and K. Yamada, J. Phys. Soc. Jpn. 81 (2012) p.034709.
[80] H. Sagayama, D. Uematsu, T. Arima, K. Sugimoto, J.J. Ishikawa, E. O’Farrell and S. Nakatsuji, Phys. Rev. B 87 (2013) p.100403(R).
[81] X. Wan, A.M. Turner, A. Vishwanath and S.Y. Savrasov, Phys. Rev. B 83 (2011) p.205101.
[82] T. Arima, J. Phys. Soc. Jpn. 82 (2013) p.013705.