Multiple magnetic order parameters coexisting in multiferroic hexaferrites resolved by soft x rays

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ABSTRACT
We investigated, by using soft x rays, one of the most fundamental properties in multiferroics, that is, coupled or decoupled feature among coexisting multiple (anti)ferroic order parameters for two types of multiferroic hexaferrites. Circular dichroic signals observed at x-ray resonance for diffraction and absorption enable us to resolve several kinds of magnetic domains, which are spatial distributions of the respective order parameters. We examined magnetic field effects on the domains and unveiled the features of the order parameters. It is found that the coupled or decoupled features of the order parameters are explained by the symmetry analysis based on the Landau theory. These findings contribute to an understanding of magnetoelectric couplings in multiferroics and to exploiting a wide variety of their functionalities. In addition, we suggest a circular dichroic specular off-peak scattering at resonance as a powerful technique for studying a surface state of a magnetic order in an expansive range of quantum materials.

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I. INTRODUCTION
Multiferroics—a class of materials exhibiting two or more simultaneous ferroic orders1 or, more recently, with extension to antiferroic orders2—have attracted considerable attention in the field of condensed matter physics due to their various intriguing physics. These are, for instance, spin-driven ferroelectricity, associated pronounced magnetoelectric effect,3 and a novel excitation, electromagnon.4 A ferroic order described by an order parameter (e.g., electric polarization and magnetization) forms a spatial distribution of an ordered state, or a domain structure, due to the presence of switchable bistability. In multiferroics, multiple order parameters can individually form domains, leading to more complicated situations and field-responses of the order parameters or domains. Observing spatial distributions of the ordered states is, therefore, significantly important to understand the functionalities of multiferroics.

Whereas observing domains formed by a ferroic order, such as a ferroelectric, ferromagnetic, or ferroelastic one, is relatively straightforward, observing those formed by an antiferroic order, such as an antiferromagnetic one, is a challenging issue. However, recent extensive studies on magnetoelectric multiferroics, which typically exhibit simultaneous ferroelectric and antiferromagnetic orders, have expanded the demand for the observation of antiferromagnetic domains. Indeed, such a demand has developed various experimental techniques, e.g., optical second-harmonic generation, neutron topography, spin-polarized scanning microscopy, and resonant x-ray diffraction.5 Such techniques have revealed non-trivial responses and couplings among coexisting order parameters in multiferroics. Examples are (i) shared domain walls between two distinct order parameters,6,7 (ii) formation of charged domain walls associated with a magnetic phase transition despite their energy cost8,9 (iii) control of a domain pattern through a cross coupling
effect, and (iv) an intact domain pattern at flipping an order parameter despite random nucleation/movements of domain walls through full volume of the material. These findings indicate that couplings among coexisting order parameters lead to unique phenomena in this class of materials.

The coupled feature between two order parameters enables us to switch their signs simultaneously [see Figs. 1(b)–1(d)]. On the other hand, the decoupled feature enables us to switch among four possible states [see Figs. 1(a)–1(c)]. To uncover these features, resolving individual domains formed by coexisting order parameters is the most direct and ideal approach. Soft x-ray diffraction is one of the most powerful techniques to reveal such features through disentangling coexisting order parameters with different diffraction conditions.

In this article, we show our observations of multiple kinds of magnetic domains coexisting in two multiferroic hexaferrites: Y-type hexaferrite $\text{Ba}_{1.3}\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$ and Z-type hexaferrite $\text{Sr}_{3}\text{Co}_{2}\text{Fe}_{24}\text{O}_{41}$. The former has two kinds of antiferromagnetic domains, and the latter has two kinds of ferromagnetic domains and one kind of antiferromagnetic domain. Resonant x-ray diffraction and x-ray magnetic circular dichroism (XMCD) are utilized to resolve the magnetic domains in these hexaferrites. Resolving domains, of which pattern changes with a magnetic field, can clearly uncover coupled or uncoupled features among the order parameters. Such features are corroborated by the symmetry analysis based on the Landau theory.

II. RESULTS AND DISCUSSION

We performed soft x-ray experiments on single crystals of the two types of hexaferrites, $\text{Ba}_{1.3}\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$ and $\text{Sr}_{3}\text{Co}_{2}\text{Fe}_{24}\text{O}_{41}$, at the BL17SU in SPring-8. These crystals with a cleaved surface normal to the hexagonal [001] direction are the same with those used in Refs. 13 and 16. The crystals were mounted on a four-circle diffractometer implemented in the beamline so that [001], which is normal to the surface, is along a scattering vector $\mathbf{Q}$ of a specular reflection. All data shown in this article were taken at room temperature. We applied a magnetic field in the basal plane with a Nd magnet ($\approx 0.2$ T) to investigate a magnetic field effect on antiferromagnetic domains for Y-type $\text{Ba}_{1.3}\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$ and along [100] ($a$ axis) with a pair of SmCo magnets ($\approx 0.3$ T) during both resonant diffraction and absorption measurements to fix the in-plane magnetization for Z-type $\text{Sr}_{3}\text{Co}_{2}\text{Fe}_{24}\text{O}_{41}$. Note that all measurements of the Y-type hexaferrite were performed in zero magnetic field. Signals for x-ray diffraction were collected by a Si photodiode, and those for absorption were collected by the total electron yield with a normal x-ray incidence to the sample surface. Both signal currents were measured by a picoammeter (Keithley 6514). Energy of an incident x-ray beam is around the Fe $L_2,3$ edges, and the size of the beam is focused to $\approx 30 \times 15 \mu$m$^2$, which is small enough to map the magnetic domains of these hexaferrites. The circularly polarized state of an incident x-ray beam is described by the Stokes parameter $P_2$, which is +1 for right and −1 for left.

A. Y-type hexaferrite $\text{Ba}_{1.3}\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$

The Y-type hexaferrite $\text{Ba}_{1.3}\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$ has a space group $R3m$ with lattice parameters $a \approx 5.9$ Å and $c \approx 43.4$ Å [see Fig. 2(a)]. The crystal structure is composed of two block layers $L$ and $S$, which alternately stack along [001]. Each of the block layers is assumed to have a magnetic moment $\mu_L$ and $\mu_S$, respectively. The magnetic structure at room temperature and zero magnetic field is the so-called alternating longitudinal conical (ALC) structure [see
FIG. 2. Crystal and magnetic structures of the Y-type hexaferrite Ba$_{1.3}$Sr$_{0.7}$CoZnFe$_{11}$AlO$_{22}$. (a) The crystal structure viewed along [110]. (b) A schematic of the alternating longitudinal conical (ALC) structure. Here, the magnetic structure is represented by employing a conventional block-spin approximation, where two magnetic blocks, termed L and S blocks, alternately stack along [001]. The ALC structure is composed of a helical component in the basal plane (c) and (d) and an antiferromagnetic component along [001] [(e) and (f)]. Red and blue arrows in (b)–(f) denote the magnetic moments in L and S blocks, respectively. The crystal structure is drawn by using VESTA.

The ALC structure, represented by $\mu_L$ and $\mu_S$, is composed of two antiferromagnetic components. One is an in-plane helical component with an incommensurate modulation vector $\mathbf{k} = (0,0,\delta)$, where $\delta$ is a non-integer. The component is illustrated in Figs. 2(c) and 2(d), which correspond to two spin-chiral domain states described by the sign of vector spin chirality $C$, +1 (right) and −1 (left). The other is an out-of-plane $\uparrow\downarrow\downarrow\uparrow$ collinear antiferromagnetic component with a commensurate modulation vector $\mathbf{k} = (0,0,1.5)$. The component is illustrated in Figs. 2(e) and 2(f), which correspond to two antiferromagnetic domain states described by the sign of antiferromagnetic phase $\Delta$, +1 (↑↑↑↑) and −1 (↑↑↑↓). Thus, there are two magnetic order parameters $C$ and $\Delta$ in this magnetic structure. The latter parameter gives rise to electric polarization along [001] (P$_{[001]}$) through exchange striction, and, hence, the ALC phase is multiferroic.

1. Resonant diffraction profile

The resonant diffraction profiles along 00L from the Y-type hexaferrite Ba$_{1.3}$Sr$_{0.7}$CoZnFe$_{11}$AlO$_{22}$ is shown in Fig. 3. Two families of superlattice reflections are visible at 003 ± $\delta$ (incommensurate) and 003 ± 1.5 (commensurate) in addition to the 003 Bragg reflection. Here, in the description of the reflection index 003 ± $\delta$ or 003 ± 1.5, the number on the underline corresponds to the L component. These reflections are consistent with the ALC structure. The incommensurate reflections correspond to the order of the in-plane helical component, and the commensurate reflection corresponds to that of the out-of-plane $\uparrow\downarrow\downarrow\uparrow$ antiferromagnetic component. Negligible XMCD profile, absence of circular dichroism on the 003 Bragg reflection [see Figs. 9 and 3(b), respectively], and zero magnetization at 0 T indicate the absence of a ferromagnetic order. These results also exclude a possible mixed phase with a ferromagnetic structure and support the ALC structure. Additional high-order incommensurate reflections, e.g., 004δ and 006 − 2δ, are seen in the profile [see the dotted lines in Fig. 3(a)]. Among several possible origins, unlike in rare-earth magnets and multiferroics, a magneto-elastically induced lattice modulation with $\mathbf{k} = (0,0,2\delta)$ in this material is negligible as not observed in an electron diffraction profile. Accordingly, orbital modulation caused by spin-dependent orbital hybridization is also negligible. The higher-order reflections are probably caused by a magnetic scattering due to the helical component. They can appear as a result of either a distortion in the helical component as found in anisotropic rare-earth magnets and multiferroics or additional contribution from high-order terms of an electric–dipole or electric–quadrupole resonant transition. The penetration depth of the x-ray beam estimated from the full width at half maximum of the 003 Bragg reflection is ~60 nm.

The superlattice reflections 003 ± $\delta$ and 003 ± 1.5 show clear circular dichroism on their intensities as seen in Figs. 3(c) and 3(d) in contrast to the 003 Bragg reflection shown in Fig. 3(b). The circular dichroism on the incommensurate reflection is reasonably ascribed to a pure magnetic scattering as reported for other Y-type hexaferrites that exhibit an incommensurate helical order without any additional ferromagnetic or antiferromagnetic component. The circular dichroic part in the diffraction intensity $d\sigma/d\Omega|_{p_{ij}}$ of the incommensurate reflection is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{p_{ij}} = 4P_{2}CN^{2}|b|^2 \cos \theta \sin 2\theta,$$

where $N$ is the number of unit cells contributing to the scattering and $\theta$ is the Bragg angle. The coefficient $b$ is...
the coefficient of the first-order magnetic scattering term appearing in the resonant elastic scattering length through an electric–dipole transition. Here, \( q \) is the wave vector of an incident x-ray beam and \( F_\nu \) is the resonant strength of the electric–dipole transition with a change 1 in orbital quantum number and a change \( \nu \) in magnetic quantum number. Equation (1) clearly indicates that the circular dichroism corresponds to vector spin chirality \( C \) in the helical component.

On the other hand, the circular dichroism on the commensurate reflection is not explainable by a simple magnetic scattering but by an interference effect between two scatterings, i.e., charge and magnetic scatterings. These scatterings overlap each other with the same modulation vector \( k = (0,0,1.5) \) caused by the ↑↑↓↓ antiferromagnetic component. Indeed, such a charge scattering was detected at the family of the commensurate reflections with \( k = (0,0,1.5) \), 00\( \pm \delta \) (\( \delta \) an integer), in Ba\( _{1.3} \)Sr\( _{0.7} \)CoZnFe\( _{11} \)AlO\( _{22} \) by an electron diffraction measurement. With the presence of the interference effect, the circular dichroic part in the diffraction intensity of the commensurate reflection is given by

\[
\frac{d\sigma}{d\Omega} = 2P_2|\Delta\mu_0 \cos\alpha m(a'b') + \mu_1 \cos\beta Re(a'b')|z \cdot (\vec{q} + \vec{q'} \cos 2\theta).
\]

(2)

Here, \( \alpha (\beta) \) is the half opening angle of the conical structure of an \( S (L) \) block. The coefficient \( a \) is the crystal structure factor at the scattering vector \( Q = (0,0,4.5) \), and \( z \) and \( \vec{q} (\vec{q'}) \) are unit vectors along [001] and the wave vector of an incident (scattered) x-ray beam, respectively. Equation (2) indicates that the circular dichroism corresponds to \( \Delta \) in the ↑↑↓↓ antiferromagnetic component. Thus, circular dichroic signals on the two families of superlattice reflections 00\( \pm \delta \) and 00\( \pm 1.5 \) individually resolve magnetic domains formed by vector spin chirality \( C \) and those formed by antiferromagnetic phase \( \Delta \).

2. Domain observation and symmetry analysis

Scanning with the circularly polarized and focused x-ray beam at the superlattice reflections enables us to visualize real-space magnetic domains. Figure 4 shows two-dimensional maps of the diffraction intensities plotted as the flipping ratio (FR) \( \frac{(I_{++} - I_{-+})}{(I_{++} + I_{-+})} \), that is, the normalized difference of the diffraction intensities measured with left- and right-circularly polarized incident x-ray beams. Here, the subscript means the Stokes parameter \( P_2 \). It is clear that the two magnetic order parameters in the ALC structure, i.e., \( C \) (incommensurate component) and \( \Delta \) (commensurate component), individually form inhomogeneous magnetic domains and do not share any domain boundary. After a sequential procedure of applying and removing an in-plane magnetic field (≈0.2 T), which is large enough to stabilize a field-induced phase, the domain structure formed by \( C \) shows a clear change [compare Figs. 4(a)–4(c)]. This change is in contrast with the domain structure formed by \( \Delta \), which is almost intact for the magnetic field cycle [compare Figs. 4(b)–4(d)]. Hence, our investigation of a magnetic field effect on the two antiferromagnetic
domain structures clearly indicates a decoupled feature between the two order parameters, $C$ and $\Delta$, as confirmed in Ref. 16.

In order to understand the decoupled feature between the order parameters coexisting in the ALC structure of the Y-type hexaferrite $\text{Ba}_1.3\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$, we perform a symmetry analysis based on the Landau theory. A symmetry analysis gives possible coupling terms between two (or more) order parameters in the free energy. When a bilinear coupling term between two order parameters is, for instance, included in the free energy, a sign flipping in one parameter switches the sign of the other parameter so as to minimize the free energy. The order parameters that we consider here are (i) $C$, vector spin chirality; (ii) $\Delta$, antiferromagnetic phase; and (iii) $P_{[001]}$, electric polarization along [001]. Table I is a summary of their characters for the symmetry operations in space group R3m. The symmetry operations are (1) $1$, the identity operation; (2) $3$, threefold rotational operation along [001]; (3) $m$, mirror operation normal to [120]; (4) $2$, twofold rotational operation along [100]; (5) $i$, inversion operation; (6) $3$, threefold rotoinversion operation along [001]; and (7) $t$, time-reversal operation.

The irreproducible representation of a coupling term must be totally symmetric ($A_{1g}$). Among the order parameters, an allowed term is only

$$U = \Delta P_{[001]},$$

showing a bilinear coupling between $\Delta$ and $P_{[001]}$. Equation (3) phenomenologically represents an induction of the electric polarization originating from the $\uparrow\downarrow\uparrow\downarrow$ antiferromagnetic component via the exchange striction. A bilinear term between $C$ and $\Delta$ does not belong to the totally symmetric irreproducible representation. Therefore, these two order parameters decouple to each other as observed in the resonant diffraction experiments.

B. Z-type hexaferrite $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$

Z-type hexaferrite $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ has the space group $P6_3/mmc$ with lattice parameters $a \approx 5.9$ Å and $c \approx 52.3$ Å [shown in Fig. 5(a)]. The crystal structure is composed of two block layers $L$ and $S$ as in the Y-type hexaferrite $\text{Ba}_1.3\text{Sr}_{0.7}\text{CoZnFe}_{11}\text{AlO}_{22}$, but with a different motif for the $L$ block, resulting in different symmetry from Y-type hexaferrites. Each of the block layers is assumed to have a magnetic moment $\mu_L$ or $\mu_S$, as in the Y-type hexaferrite. The magnetic structure at room temperature around zero magnetic field is the conical spin-spiral structure shown in Fig. 5(b). This structure is composed of (i) a spin-spiral component with a modulation vector $k = (0,0,1)$ [Figs. 5(c) and 5(d)] and (ii) a ferrimagnetic component with a modulation vector $k = (0,0,0)$ [Fig. 5(i)]. In the conical spin-spiral structure, the ferrimagnetic component parallel to the spin-rotation axis of the spin-spiral component is off from the basal plane by an angle $\gamma$. Therefore, these two components are further decomposed into normal ones to and parallel ones to the [001] direction: (i) a cycloidal component [Figs. 5(e) and 5(f)] and a helical component [Figs. 5(g) and 5(h)] for the spin-spiral component; (ii) a normal component [Fig. 5(j), $M_{1[001]}$] and a parallel component [Fig. 5(k), $M_{2[001]}$] for the ferrimagnetic component. The magnetic order induces electric polarization in the basal plane through the inverse Dzyaloshinskii-Moriya interaction and the spin-dependent $d$-$p$ hybridization. Hence, the conical spin-spiral phase is multiferroic. A coupled feature between the helicity of the spin-spiral component and the electric polarization induced by the two mechanisms described above together with a reversal of the magnetization is crucial for the magnetoelectric effect in the Z-type hexaferrite.

1. Resonant diffraction profile

The resonant diffraction profiles along 00$L$ from the Z-type hexaferrite $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ are shown in Figs. 6(a) and 6(b) [or 7(a) for the overall profile]. Here, the profiles were taken at the diffraction geometries illustrated in the lower panels of the respective figures; a magnetic field ($\approx 0.3$ T) along [100] is normal ($\varphi = 90^\circ$) [parallel ($\varphi = 0^\circ$)] to the scattering plane for the profiles shown in

![Image](https://example.com/image.jpg)
shown in Figs. 6(a) and 7(a) is, therefore, a superlattice reflection due to the magnetic order. A finite XMCD signal with a normal magnetic field is along [100], indicating the presence of magnetic order. The scattering plane, a reflection 00\(m\) with a normal angle \(\gamma\) so that both of them are decomposed into two components. For the spin-spiral component [(c) and (d)], a cycloidal component [(e) and (f)] and a helical component [(g) and (h)] of which the spin-rotation axis is (c), (e), and (g)] normal to and \((d), (f), (h)\) parallel to the [001] axis. For the ferrimagnetic component (i), two ferrimagnetic components whose moment is (j) normal to or (k) parallel to the [001] axis. Red (blue) arrows in (b)–(k) and \(\beta (\alpha)\) denote the magnetic moments and the half opening angle of the conical structure in an L (S) block, respectively. Green arrows in (b) and (i)–(k) denote magnetization emerged by the uncompensated magnetic moments between L and S blocks. The crystal structure is drawn by using VESTA.46

Figs. 6(a) and 7(a) [Fig. 6(b)], termed diffraction geometry.1,2 The magnetic field is fixed along [100] and is rotated with the azimuthal angle \(\varphi\), which is defined as an angle between [100] and the scattering plane. A reflection 00\(L\) for space group \(P6_3/mmc\) is allowed for an even integer \((L = 2n)\) and forbidden for an odd integer \((L = 2n - 1)\), where \(n\) is an integer. The reflection 003 shown in Figs. 6(a) and 7(a) is, therefore, a superlattice reflection due to the magnetic order. A finite XMCD signal with a normal x-ray incidence to the basal plane is observed [see Fig. 6(a)] though the magnetic field is along [100], indicating the presence of magnetization along [001]. This is in contrast with the Y-type hexaferrite \(Ba_{1.3}Sr_{0.7}CoZnFe_{11}AlO_{22}\) shown in Fig. 2(b). The spin-rotation axes of (c) and (d) and the magnetization in (i) lift from the basal plane by \(\gamma\) so that both of them are decomposed into two components. For the spin-spiral component [(c) and (d)], a cycloidal component [(e) and (f)] and a helical component [(g) and (h)] of which the spin-rotation axis is (c), (e), and (g)] normal to and \((d), (f), (h)\) parallel to the [001] axis. For the ferrimagnetic component (i), two ferrimagnetic components whose moment is (j) normal to or (k) parallel to the [001] axis. Red (blue) arrows in (b)–(k) and \(\beta (\alpha)\) denote the magnetic moments and the half opening angle of the conical structure in an L (S) block, respectively. Green arrows in (b) and (i)–(k) denote magnetization emerged by the uncompensated magnetic moments between L and S blocks. The crystal structure is drawn by using VESTA.46

There are three characteristics in the resonant diffraction profiles: (i) significant circular polarization dependence on both the 003 and 004 reflections [see Figs. 6(a) and 6(b)], (ii) circular polarization dependent asymmetry around the reflections [see Figs. 6(a) and 7(a)], and (iii) significant circular polarization dependence in specular but off-peak scatterings [see Fig. 7(a)]. At first, we refer to

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right)_{\mu} = -4NP_{2}\text{Im}(a'b)\left[ \cos \gamma (\mu_{L}\cos \beta - \mu_{S}\cos \alpha) \cos \varphi \cos^{3}\theta + \sin \gamma (\mu_{L}\cos \beta - \mu_{S}\cos \alpha) \sin^{3}\theta \right]
= -4NP_{2}\text{Im}(a'b)[M_{L[001]} \cos \varphi \cos^{3}\theta + M_{S[001]} \sin^{3}\theta],
\]

where \(M_{L[001]} = \cos \gamma (\mu_{L}\cos \beta - \mu_{S}\cos \alpha)\) is the ferrimagnetic component normal to the [001] direction and \(M_{S[001]} = \sin \gamma (\mu_{L}\cos \beta - \mu_{S}\cos \alpha)\) is that parallel to [001]. The diffraction geometry 2 corresponds to \(\varphi = 0^\circ\), and the circular dichroism shown in Fig. 6(b) is mainly due to the first term as a sign flipping in \(M_{L[001]}\) changes the sign of the circular dichroism,53 whereas that in \(M_{S[001]}\) does not (shown in later). Equation (4) clearly shows that the circular dichroism corresponds to the magnetization \(M_{L[001]}\) and \(M_{S[001]}\) as the circular dichroic terms are proportional to the sign of \(M_{L[001]}\) and \(M_{S[001]}\). Although the circular dichroism on the magnetic reflection due to the spin-spiral order in the Y-type hexaferrite
$Ba_{1.3}Sr_{0.7}CoZnFe_{11}AlO_{22}$ (see Sec. I) as other helimagnets\cite{30,31,37} is
ascribed to a pure magnetic scattering, the one on the 003 superlat-
tice reflection from the Z-type hexaferrite is not explainable only
by a pure magnetic scattering. This is evident when one considers
the azimuthal angle dependence of the circular dichroic part in the
diffraction intensity of the 003 Bragg reflection from a pure mag-
netic scattering formulated as

$$\left( \frac{d\sigma}{d\Omega} \right)_{P_2} = 4P_2CN^2|b|^2 \sin \alpha \sin \beta \sin 2\theta (\cos \gamma \sin \theta \cos \varphi + \sin \gamma \cos \theta).$$

\hspace{2cm} (5)

The first term in the bracket is caused by the cycloidal com-
ponent whose spin-rotation axis is normal to [001] [see Figs. 5(e)
and 5(f)], and the last one in the bracket is caused by the helical
component whose spin-rotation axis is parallel to [001] [see
Figs. 5(g) and 5(h)]. The contribution from the first term is sig-
nificant when $\varphi = 0^\circ$ or $180^\circ$ but is not significant when $\varphi = 90^\circ$
while the last term is independent of \( \varphi \). Hence, it is expected that the circular dichroism is more prominent at \( \varphi = 0^\circ \) or \( 180^\circ \) than at \( \varphi = 90^\circ \). We have, however, found that the relation is opposite [compare Figs. 6(a) and 10]. This implies that an additional contribution exists and that it interferes with the magnetic scattering as well as the 004 reflection. Indeed, a charge scattering is observed at \( 002n - 1 \) in Z-type hexaferrites,\(^5,26\) which means the occurrence of a symmetry lowering. A magnetic field (or the ferrimagnetic component) along [100] can induce a lattice distortion through magnetostriction and makes the symmetry lower into \( Cmcm \), but \( 002n - 1 \) is still forbidden. Thus, a further symmetry lowering with which \( 002n - 1 \) gets allowed is expected in the conical spin-spiral phase though further investigation is required to clarify the exact symmetry. Taking the isotropic charge scattering into account, the circular dichroic part in the diffraction geometry is

\[
\left( \frac{d\sigma}{d\Omega} \right)_I = 4P_2CN\text{Re}(a' b) \sin \beta \cos^3 \theta \sin \varphi + 4P_2N \sin \alpha \text{Im}(a' b) \sin \gamma \cos^3 \theta + CN|b|^2 \sin \beta \cos \gamma \sin \theta \sin 2\theta \cos \varphi \\
+ 4P_2N \sin \alpha \left[ -\text{Im}(a' b) \cos \gamma \sin^3 \theta + CN|b|^2 \sin \beta \sin \gamma \cos \theta \sin 2\theta \right].
\]

(6)

Here, the circular dichroism, which corresponds to vector spin chirality \( C \) of the spin-spiral component, appears at three terms. These terms are consistent with our observation, e.g., more prominent circular dichroism at \( \varphi = 90^\circ \) than at \( \varphi = 0^\circ \) or \( 180^\circ \) and observed azimuthal angle dependence of the circular dichroism.\(^1,3\)

We now argue for points (ii) and (iii), the circular polarization dependent asymmetry around the reflections and circular dichroic specular off-peak scatterings, respectively. A specular x-ray scattering can be ascribed to optical reflection from the surface, or, in other words, an x-ray crystal truncation rod (CTR) scattering due to a sharp termination of a crystal lattice. The circular dichroism indicates the presence of an interference between scattered beams, and the asymmetry observed around the reflections indicates a sign flipping in either of the scattered beams across the reciprocal points. Since a CTR scattering changes its phase by \( \pi \) at reciprocal points, the asymmetry of the profile is most likely ascribed to the interference involving it. The CTR scattering amplitude for a reciprocal point \((H,K,L)\) is

\[
F_{\text{CTR}} = F_{\text{HR}}(L) \sum_{n=-1}^{N-1} \exp(2\pi inL) \\
= F_{\text{HR}}(L) \frac{\sin(\pi NL)}{\sin(\pi L)} \exp[\pi i(N - 1)L],
\]

(7)

where \( F_{\text{HR}}(L) \) is the scattering amplitude from one atomic layer of a crystal. One finds that the imaginary part of the last factor changes its sign when \( L \) goes across a reciprocal lattice point, i.e., where \( L \) is an integer, while the real part of the factor does not. Thereby, an interference between the CTR scattering and another scattering or between two CTR scatterings can create an asymmetric profile around the reflections.

The Z-type hexaferrite specimen is a single crystal, but there are two scattered beams: one is from a charge scattering and the other is from a magnetic scattering. Thus, point (ii), the asymmetric profile across the reflections, is reasonably explained through the interference between charge/magnetic CTR scatterings. The circular dichroism originates from a magnetic part of the CTR scatterings. Besides, a CTR scattering gives finite intensities along the surface normal between Bragg reflections, i.e., along 00L in the Z-type hexaferrite. Point (iii) is also caused by the presence of the interference between the two CTR scatterings at specular but off-peak positions.

Our simulation taking charge/magnetic CTR scatterings from the Z-type hexaferrite \( \text{Sr}_5\text{Co}_2\text{Fe}_{24}\text{O}_{41} \) into account reproduces well the profiles with all the points (i)–(iii) as shown in Fig. 7(b) [compare with Fig. 7(a)]. In the calculation, we assume (1) that the crystal structure has the perfect basal plane surface terminated at the center of an \( L \) block without any roughness and (2) that the magnetic structure is as shown in Fig. 5(b) at \( \varphi = 90^\circ \). Here, we do not take any lattice modulation emerging from the 00odd reflections (see above discussion) into account. In terms of point (i), it is noted that the circular dichroism on the 00odd and 00even reflections at \( \varphi = 90^\circ \) is ascribed to the in-plane helical component [Figs. 5(g) and 5(h)] and the ferrimagnetic component along [001] [Fig. 5(k)], respectively [see Eqs. (6) and (8), respectively]. Both of the components appear due to the tilting of the spin-rotation axis from the basal plane. In this simulation, we have confirmed that a switching in the helicity of the spin-spiral component roughly inverts the circular dichroism especially around the 00odd reflections, which appear due to the spin-spiral component [see Fig. 12].

A scattering from a surface appears more prominently in soft x-ray regime than in hard x-ray regime because any scattering occurs near the surface due to the small penetration depth of an incident x-ray beam. However, a sharp termination of a lattice plane is required for a CTR scattering to have a finite intensity and to interfere with the other. We measured the surface roughness of the Z-type hexaferrite specimen used in the soft x-ray regime by atomic force microscopy and found that this is less than 1 nm [see Fig. 11(a)], which is good enough for a CTR scattering to have a finite intensity.

2. Domain observation

The circular dichroism on the superlattice reflections and XMCD enables us to resolve real-space magnetic domains by taking two-dimensional maps of the signals. A two-dimensional

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distribution of XMCD signal was taken with normal x-ray incidence to the basal plane surface. It shows a clear contrast (positive and negative) [see Fig. 8(c)], corresponding to ferrimagnetic domains whose magnetization is along [001] [see Fig. 5(k)]. On the other hand, the circular dichroism of the 004 reflection, which is ascribed to the two ferrimagnetic components as shown by Eq. (4), exhibits a homogeneous two-dimensional profile in terms of the sign of FR (negative) with a small fluctuation as seen in Fig. 8(b). These two-dimensional profiles are well explained when the in-plane ferrimagnetic component [see Fig. 5(i)] is homogeneous with a single domain while the out-of-plane ferrimagnetic component is inhomogeneous with multidomains. The domain wall of the out-of-plane component indicated by a gray curve in Fig. 8(b) matches well with a small change in FR of 004 as shown in Fig. 8(f). This small change is due to a sign reversal of the out-of-plane component across the boundary and indicates smaller contribution of the second term in Eq. (4) than the first term. From Eq. (4), we can estimate the tilt angle $\gamma$ as $\approx 7^\circ$.

![Image of two-dimensional profiles](image-url)

**FIG. 8.** Real-space two-dimensional (c) XMCD and FR profiles obtained at 003 [(a) and (d)] and 004 [(b) and (e)] from the basal plane surface of the Z-type hexaferrite $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$. The FR profiles were taken in the diffraction geometries shown in Fig. 6 for the respective reflections, and the XMCD profile was taken with a normal x-ray incidence to the basal plane surface. After taking the profiles of (a)–(c), the magnetic field direction was tilted a bit toward out of the basal plane (see text), and the profiles of (d) and (e) were subsequently taken. A gray curve in (a) and (b) shows a boundary between positive and negative XMCD signals in (c) around the upper part of the specimen. (f) Vertical one-dimensional profiles of XMCD (black) and FR (003: red, 004: blue) across the boundary along the white dotted lines in (a)–(c). The region out of the specimen is white-colored or shown with a mottled pattern.
TABLE II. Eigenvalues and irreducible representations of the order parameters in the conical spin-spiral phase of the Z-type hexaferrite for the symmetry operations of space group \( \text{P6}_3/mmc \).

<table>
<thead>
<tr>
<th>Order parameter</th>
<th>Eigenvalue</th>
<th>Irreducible representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_{1[001]} )</td>
<td>1 1 −1 1 −1 1 −1 1 −1 −1 −1</td>
<td>( B_{1g} )</td>
</tr>
<tr>
<td>( M_{1[001]} )</td>
<td>1 1 1 −1 −1 −1 1 1 1 1 1</td>
<td>( A_{2g} )</td>
</tr>
<tr>
<td>C</td>
<td>1 1 −1 1 −1 −1 1 −1 −1 1 1</td>
<td>( B_{2u} )</td>
</tr>
</tbody>
</table>

The circular dichroism of the 003 reflection, which directly reflects the helicity of the spin-spiral component, exhibits inhomogeneous distribution (positive and negative), i.e., a multi-domain state [see Fig. 8(a)]. The distribution is more complex than the ferrimagnetic domains. A small change related to the sign reversal of the out-of-plane component is also visible in FR of 003. This change is ascribed to the terms caused by the in-plane helical component [Figs. 5(g) and 5(h)] proportional to \( \sin \theta \) in Eq. (6) with \( \varphi = 90^\circ \).

After taking the images shown in Figs. 8(a)–8(c), a magnetic field direction was tilted a bit toward out of the basal plane to align the out-of-plane ferrimagnetic component as well as the in-plane one. As a result, a homogeneous two-dimensional FR profile of the 004 reflection was observed as shown in Fig. 8(e). It guarantees the single domain state for both the ferrimagnetic components. On the other hand, the two-dimensional FR profile of the 003 reflection is intact by aligning of the out-of-plane ferrimagnetic component [compare Figs. 8(a) and 8(d)]. It means that the out-of-plane ferrimagnetic component is reversible in space without change in the spin-spiral component and the in-plane ferrimagnetic component. In the other words, the out-of-plane ferrimagnetic component decouples from the spin-spiral component and the in-plane ferrimagnetic component [see Figs. 1(a) and 1(c)]. This is in contrast with the coupled feature between the in-plane ferrimagnetic component and the spin-spiral component; a sign reversal in the in-plane ferrimagnetic component always accompanies a sign reversal in the spin-spiral component [see Figs. 1(b) and 1(d)].

C. Symmetry analysis

In order to understand the decoupled feature between the order parameters coexisting in the conical spin-spiral structure of the Z-type hexaferrite \( \text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41} \), we perform the symmetry analysis based on the Landau theory. The order parameters that we consider here are (1) \( M_{1[001]} \), magnetization normal to [001] (along [100]); (2) \( M_{2[003]} \), that along [001]; and (3) C, the helicity of the spin-spiral component whose cycloidal component is spanned by a plane normal to [100]. The discussion for the other parameters, e.g., electric polarization appearing in the conical spin-spiral phase and the toroidal moment, is in Ref. 13, and we now focus on the order parameters directly measured by the soft x-ray experiments. Table II summarizes characters of the order parameters for the symmetry operations in space group \( \text{P6}_3/mmc \). The symmetry operations are (1) 1, the identity operation; (2) 3, threefold rotational operation along [001]; (3) \( 6_3 \), sixfold screw operation along [001]; (4) \( m_{100} \), mirror operation normal to [100]; (5) \( c_g \), glide operation normal to [120]; (6) \( 2_{100} \), twofold rotational operation along [100]; (7) \( 2_{120} \), that along [120]; (8) I, inversion operation; (9) 3, threefold rotoinversion operation along [001]; (10) 6, sixfold rotoinversion operation along [001]; (11) \( m_{001} \), mirror operation normal to [001]; and (12) \( t \), time-reversal operation.

None of a coupling term among these three order parameters belongs to the totally symmetric irreducible representation (\( A_1 \)). The absence of a coupling term phenomenologically explains the decoupled feature between them as demonstrated in the soft x-ray experiments. Since symmetry can allow a coupled feature between two magnetization along different directions, even the decoupled feature between \( M_{1[001]} \) and \( M_{2[003]} \) is not trivial. Due to the decoupled feature, therefore, the Z-type hexaferrite \( \text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41} \) has a promising possibility as a multilevel and nonvolatile magnetic storage.

III. CONCLUSION

We revealed the decoupled features among multiple magnetic order parameters in two types of multiferroic hexaferrites through visualizing magnetic domains corresponding to respective order parameters by using soft x rays. The symmetry analyses substantiate the decoupled features. In the case of multiferroic hexaferrites, the determination of a full magnetic structure is effective to clarify their magnetoelectric-coupling mechanism as other multiferroic systems, but in reality, it is difficult due to their complex crystal and magnetic structures. Our approach based on the individual observation of multiple domains combined with the symmetry analysis gives insights into the mechanism beyond measurements of macroscopic magnetoelectric properties.

Besides, we found an asymmetry around the reflections and circular dichroic specular but off-peak scatterings in resonant diffraction profiles. These characteristics are well explained by the occurrence of an interference between charge/magnetic CTR scatterings. A charge CTR scattering and the resulting interference effect associated with it are sensitive to a termination lattice plane (see Fig. 13). Once the termination lattice plane is defined, however, the interference effect assigns well the magnetic domain state at the surface. In the present study, we neglect the depth profile of magnetization in our analysis of the CTR scatterings. In principle, however, we can involve the depth profiling after crystallographic etching, which is one of the advantages of the present technique. In depth profiling, the interference effect can be a principle of a powerful technique for visualizing magnetic domains corresponding to respective order parameters.
surface magnetism or general magnetism with a well-defined termination lattice plane.\textsuperscript{40,41}

It is widely accepted that a coupled feature between coexisting order parameters is characteristic, and attractive physics of multiferroics, which, in turn, suggests that a decoupled feature between the order parameters, is also not trivial in multiferroics. Such coupled or decoupled features discussed through direct observation of domains were reported in multiferroics with ferroelectric and ferroelastic orders,\textsuperscript{42,43} and ferromagnetic and ferroelastic orders.\textsuperscript{44,45} Developments in domain observation techniques, nowadays, have extended the range of the investigation to multiferroics with ferroelectric and magnetic orders. Our study contributes to the understanding of fundamental properties in multiferroics with complex magnetic orders that are crucial for practical applications such as multilevel storage devices. Furthermore, the techniques using circularly polarized soft x rays will be applied to the study on topological configurations of electric and magnetic polarization such as domains, skyrmions, and vortices.

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APPENDIX A: X-RAY ABSORPTION SPECTRA FROM THE Y-TYPE HEXAFERRITE Ba\textsubscript{1.3}Sr\textsubscript{0.7}CoZnFe\textsubscript{11}AlO\textsubscript{22} WITH CIRCULARLY POLARIZED X RAYS

X-ray absorption spectra from the Y-type hexaferrite Ba\textsubscript{1.3}Sr\textsubscript{0.7}CoZnFe\textsubscript{11}AlO\textsubscript{22} taken at room temperature under zero magnetic field with a normal x-ray incidence to the basal plane surface (Fig. 9).

APPENDIX B: RESONANT DIFFRACTION PROFILES FROM THE Z-TYPE HEXAFERRITE Sr\textsubscript{3}Co\textsubscript{2}Fe\textsubscript{24}O\textsubscript{41}

Resonant diffraction profiles around 003 along 00L from the Z-type hexaferrite Sr\textsubscript{3}Co\textsubscript{2}Fe\textsubscript{24}O\textsubscript{41} taken at the in-plane magnetic field angle (a) $\varphi = 0^\circ$ and (b) $+180^\circ$ (see main text). Red and blue curves represent the data obtained with right- and left-circularly polarized x rays, respectively.

APPENDIX C: SURFACE STATE CHARACTERIZATION OF THE Z-TYPE HEXAFERRITE Sr\textsubscript{3}Co\textsubscript{2}Fe\textsubscript{24}O\textsubscript{41}

Flatness at the basal plane surface of the Z-type hexaferrite specimen used in the soft x-ray experiment was confirmed by a...
dynamic-mode atomic force microscope (SPM-9700HT, Shimadzu Coop.) at room temperature and zero magnetic field. Figures 11(a) and 11(b) show the height and phase images, respectively, taken in the same region on the surface of the specimen. Bright spots in Fig. 11(a) indicate aggregation with the height of $\sim 7$ nm atop the specimen. The positions of these spots completely overlap dark spots in the phase image [Fig. 11(b)], indicating that viscoelasticity of these spots is different from the sample surface. This result suggests that the bright spots in the height image are not due to the intrinsic roughness of the specimen but due to the contamination of the dust attached during the storage. Thus, these images clearly show the small roughness at the surface (root mean square roughness: $\sim 730$ pm, three dimensional roughness average: $\sim 360$ pm), which is significantly smaller than the wavelength of an x-ray beam at the Fe $L_3$ edge ($\approx 1.7$ nm).

**APPENDIX D: CALCULATION OF RESONANT DIFFRACTION PROFILES WITH CHARGE/MAGNETIC CTR SCATTERINGS**

We calculated resonant diffraction profiles with taking charge/magnetic CTR scatterings into account using a self-written code. The charge scattering includes dispersion corrections for Fe, and a comparable magnetic scattering originates from an electric–dipole transition. The magnetic structure is simplified by employing the magnetic structure where each layer block has an aligned magnetic moment and each spin within a magnetic block is either parallel or antiparallel to the magnetic moment shown in Fig. 5(b). For the calculation, we consider several model structures that have a perfect termination plane normal to [001] without any roughness at different height along [001] $z$: 0, 1/4, 1/2, and 3/4 corresponding to a termination at the center of the lower $S$ block, lower $L$ block, middle $S$ block, and upper $L$ block, respectively, in Fig. 5(a). We summed up both magnetic scattering (only for Fe$^{3+}$) and charge

![Fig. 11. Atomic force microscope images of a region on the basal plane surface of the Z-type hexaferrite Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ specimen used in the soft x-ray experiment: (a) height and (b) phase images. (a) and (b) were taken in the same region.](image)

![Fig. 12. Results of resonant diffraction profiles calculated from the Z-type hexaferrite Sr$_3$Co$_2$Fe$_{24}$O$_{41}$, where the crystal structure [Fig. 5(a)] terminated normal to [001] at the center of an $L$ block and the magnetic structure [Fig. 5(b)] were employed. The profiles in (a) and (b) correspond to a different helicity state in the spin-spiral component as shown in Figs. 5(c) ($C < 0$) and 5(d) ($C > 0$), respectively.](image)
scattering amplitudes from respective atoms through the crystal. Obtained resonant diffraction profiles are shown in Figs. 12 and 13.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES


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