Ferromagnetic-type order of atomic multipoles in the polar ferrimagnetic $GaFeO_3$

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Resonant x-ray Bragg diffraction by gallium ferrate ($GaFeO_3$) at Friedel pairs of charge allowed reflections in the vicinity of the Fe K edge are presented. By use of the magnetization difference, the interference of charge diffraction with the magnetic diffraction is extracted. The study of Friedel pairs and concentrating at the pre-edge allows us to extract the effect of inversion symmetry breaking on the magnetic Fe 3d shell. The data are analyzed using a model based on atomic multipole moments which are magnetic and have no space inversion symmetry (magnetoelectric) interfering with the charge scattering. This model successfully describes data as a function of azimuthal angle and for different incident polarization and it shows that data can be directly related to the magnetoelectric dipole (toroidal) and quadrupole moments. Though the model describes most of the observations successfully, how to correctly describe the observed magnetic nonresonant intensity below the edge remains an open question.

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I. INTRODUCTION

The interaction of magnetic order with the occurrence of ferroelectric polarization has attracted significant interest in the past, and particularly since the discovery of large magnetoelectric effects in multiferroics.[1,2] One of the basic open questions in the field of multiferroics concerns the role played by the possible occurrence of multipoles which are both magnetic and electric. Such multipoles are expected to be present because space and time symmetries are violated in these systems. The toroidal moment, which is the magnetoelectric dipole moment, could act as an order parameter for the basic multiferroic property,[3] the magnetoelectric interaction. These moments might be directly responsible for the observed change of magnetic structure in multiferroics.[4,5] In its simplest form, the toroidal dipole $\mathbf{\Omega}$ can be written as a ground-state expectation value $\langle \ldots \rangle$ of the vector product of spin ($\mathbf{S}$) and position ($\mathbf{R}$) operators $\mathbf{\Omega} = \langle \mathbf{S} \times \mathbf{R} \rangle$, and is often also called the anapole moment or orbital current. The latter is often found in relation to the order parameter of the pseudogap phase of cuprate superconductors and has recently been identified in a CuO plaquet in cupric oxide.[6] These moments have the basic symmetry requirements of a multiferroic material; they are magnetic (time odd) and electric (flipping sign when a spatial inversion operation is applied; they are parity odd). The important question arises: Are these moments existing as an atomiclike property, based on overlap of wave functions of a magnetic ion on sites without inversion symmetry with their ligands, and if yes, how can we detect them and get more information on them?

In recent years, there have been several studies using resonant x-ray diffraction dealing with these magnetoelectric multipole moments localized at the atomic sites in a solid in an ordered form.[7–12] One of the most studied materials in this respect is $GaFeO_3$, a material which is both ferrimagnetic and piezoelectric. $GaFeO_3$ crystal structure is described by polar space group $Pc2_1n$ below ambient temperatures. The Fe ions are in the trivalent state and are expected to have a rather spherical electron density due to the half-filled shell $3d^5$ character, with negligible orbital magnetic moment. Its magnetic transition temperature is around 210 K and varies strongly with the Ga, Fe intersite mixing.[13] Optical[14] and x-ray absorption experiments[15] have been interpreted in terms of the occurrence of sizable magnetoelectric multipole moments.[9,11,16] This is caused by the absence of inversion symmetry at the Fe sites, which may also explain the significant orbital magnetic moment on Fe, which is extracted from x-ray magnetic circular dichroism.[17] Extracting atomic information on such magnetoelectric multipole moments and their ordering remains a clear challenge, as techniques accessing them are very scarce.

Resonant x-ray diffraction is the ideal technique and has been employed to study the magnetoelectric effect in this system. X-ray scattering experiments were triggered by the study of Arima *et al.*,[7] using a magnetization difference method on space group allowed reflections of type (0k0) with k even. They gave a first indication of the possibility to observe an atomiclike anapole moment experimentally. These data were then modeled by assuming an interference of different events, e.g., $E1$-$M1$ and $E1$-$E2$.[9] A subsequent theoretical study[18] modeled the scattering data with the FDMNES code[19] and found that there are several different multipole moments contributing. More recently, experiments have been extended to space group forbidden reflections of type (0k0) with k odd.[11,12] They have the advantage that there is neither a charge nor a magnetic dipole contribution, as the magnetic order is such that there is no magnetic scattering to these types of reflections. The residual scattering at the Fe $L_{2,3}$ and K edges can be interpreted as magnetoelectric caused by components of magnetic charge and magnetoelectric quadrupole moments and components of the magnetoelectric quadrupole and octopole moments, respectively. These experiments give information on the occurrence of these multipole moments, which are ordered in an antiferro type of order, as data are collected for space group forbidden reflections. Here we present data of charge allowed reflections on $GaFeO_3$ as a function of polarization and azimuthal angle, taken in the

vicinity of the Fe K edge, and compare them to model calculations based on atomiclike magnetoelectric multipole moments.

II. EXPERIMENTS

Stochiometric amounts of Ga_2O_3 (99.99% purity) and Fe_2O_3 ($\geqslant$99.0% purity) were thoroughly ground together and then synthesized at 1200 °C for 20 h in air with an intermediate grinding after 10 h. The powder was then compacted into a rod and sintered in a vertical tube furnace at 1350 °C for 30 h in air. Single crystals were grown under 8.5 bars oxygen at zoning rate of 2 mm/h. A single crystal was cut along the (0 1 0) surface and glued onto the copper sample holder mounted in a He flow cryostat reaching temperatures between 10 and 300 K. Resonant x-ray diffraction experiments were performed at Diamond Light Source, on Beamline I16 (Materials and Magnetism[20]). The horizontally polarized beam was monochromatized by a Si (111) channel-cut monochromator. Experiments were performed with a focus of approximately 185 $\times$ 35 μm^2 and x-ray energies in the vicinity of the Fe K edge (7.1 keV). The magnetization of the sample was changed by mounting a small electromagnet directly on the cold finger of the diffractometer and applying a field of 0.05 T along the c axis (easy magnetization direction collinear to the field). This allows us to perform azimuthal angle (ψ) scans keeping the magnetic field always along the c axis. Having the c axis in the scattering plane corresponds to $\psi = 90°$. To measure the second reflection of the Friedel pair, the sample was reglued upside down. This corresponds to a rotation of the crystal around the c axis by 180°. All experiments were performed with incident x-ray polarization normal or parallel to the plane of scattering (σ or π polarization, respectively) and without analysis of the scattered x-ray polarization. Data collections were performed with a photo avalanche diode detector and scans were performed by collecting 100 times a signal with $+$, $-$, $-$, $+$ directions of the applied magnetic field along the crystallographic c direction.

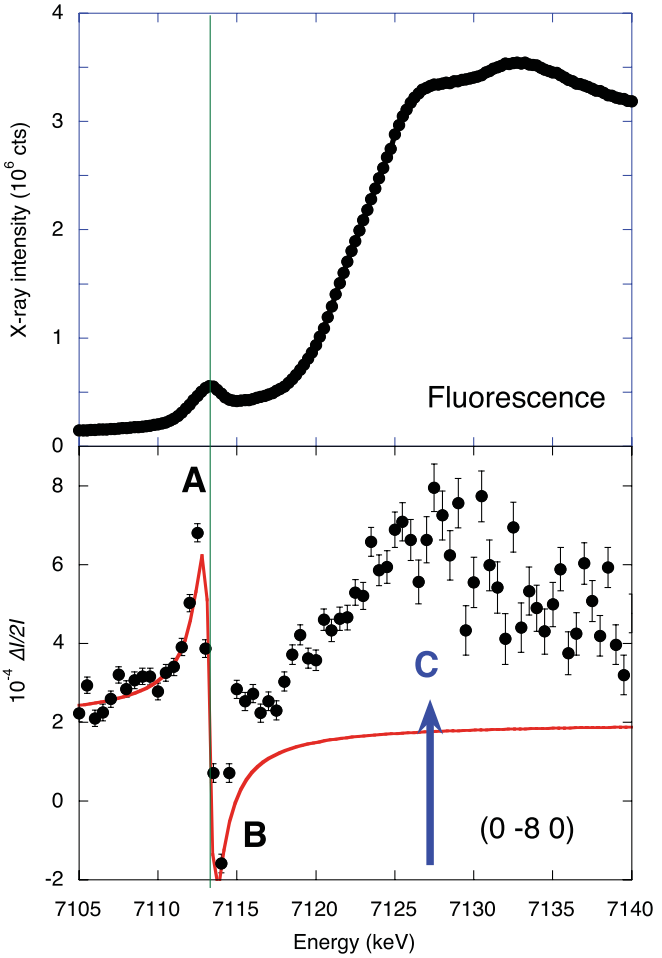

FIG. 1. (Color online) Upper part: Total fluorescence yield of $GaFeO_3$ taken in the vicinity of the Fe K edge. Lower part: $\Delta I/2I$ for the (0-80) reflection in the vicinity of the Fe K edge. Different features are labeled with A, B, and C. The solid red function reflects the theoretical description explained in the text. All data have been taken at $T = 100$ K, σ incident polarization, and at $\psi = 0°$.

III. RESULTS

To extract a magneticlike signal of a ferromagnet from a space group allowed Bragg reflection using x rays is a challenge in the hard x-ray regime. This is due to the very small enhancement factors for magnetic scattering, in particular for transition metal 3d ions. Correspondingly few studies exist. Arima has collected, with such a magnetization difference method, magnetic signals of the (020), (040), and (0-40) reflections as a function of x-ray energy. Their main experimental findings are a clear resonance observed at the pre-edge of the Fe K edge, which changes sign when going from (040) to (0-40) and a significant nonzero intensity off resonance. Figure 1 shows our normalized magnetization difference $\Delta I/2I = (I^+ - I^-)/(I^+ + I^-)$ taken at the (0-80) reflections as a function of energy together with the collected fluorescence. A similar resonance is observed at the pre-edge, and also an intensity offset in the difference.[7] On the other hand a clear intensity increase is observed at the main edge (C) as well as the resonance behavior at the pre-edge (A-B) is much sharper. The sharper resonance of the (0k0) reflection for $k = -8$ compared to those of $k = -4$, 4, and 2, is possibly intrinsic, as both experiments are supposed to have similar energy resolutions. The other difference to the data reported by Arima *et al.*[20] is the intensity increase at the Fe main K edge (C) in Fig. 1. Though the errors are significantly enlarged as the Bragg reflections are strongly suppressed by absorption at the main K edge, $\Delta I/2I$ should be intrinsically corrected for any energy-dependent absorption effects.

To gain more insight we collected the azimuthal-angle dependence of the Friedel pair reflections of (0 $\pm$ 80), which are shown in Fig. 2. The observed $\Delta I/2I$ follows for the resonant energy of 7112 eV (A in Fig. 1) a clear cosψ dependence, with an overall phase difference of π within the $k = 8$ and -8 Friedel pair. The intensity $\Delta I/2I$ at the dip energy, at 7114 eV (B in Fig. 1), is negligible and constant for all azimuthal angles as also shown in Fig. 2. This indicates that the intensity below and above the edge (A-B) is indeed not an artifact.

To visualize better the resonant shape and possibility for the interference of scattering, we show an enlarged energy

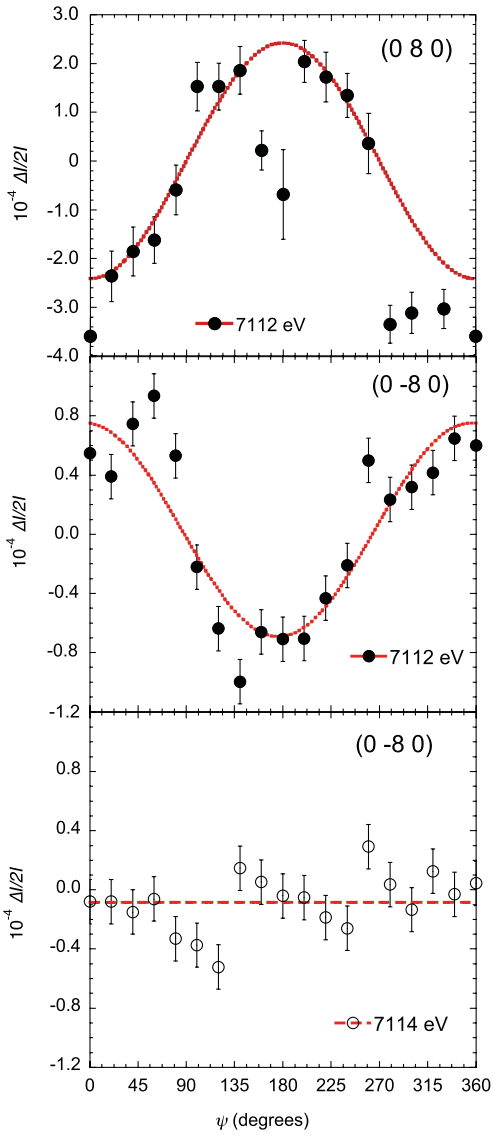

FIG. 2. (Color online) Magnetic contribution of the azimuthal-angle dependence of the Friedel pair reflections (0 ± 80) taken with the field difference method, $\Delta I/2I = (I^+ - I^-)/(I^+ + I^-)$. The upper two graphs are taken at the resonance feature A (7112 eV) whereas the bottom graph at the resonance feature B of the energy scan shown in Fig. 1. Data have been taken at $T = 100$ K and σ incident polarization.

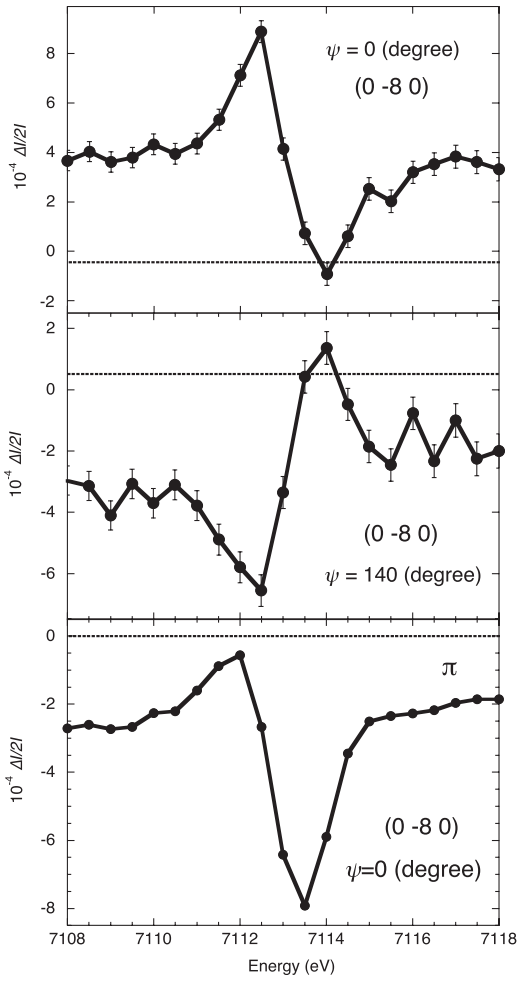

FIG. 3. Energy dependence of $\Delta I/2I$ of the (0-80) reflection taken at $T = 100$ K. Top and middle panels use σ incident polarization and differ in azimuthal angle ψ by 140°. Top and bottom panels use the same ψ and differ in use of the incident polarization, σ and π, respectively. Intensity differences $\Delta I/2I$ are mostly positive in the top panel and mostly negative in the middle and bottom panels.

scan of the (0-80) reflection for two different azimuthal angles collected in Fig. 3. These figures show that the resonant intensity and the scattering above and below the pre-edge both have a change in sign, for a change of ψ approaching 180°. The sign change is not only visible at the maxima and minima of the scattering, as expected from Fig. 2, but also below and above the sharp resonant feature.

Figure 4 shows the normalized magnetization difference $\Delta I/2I$ of the (0-80) reflection with π incident radiation together with the sum $(I^+ + I^-)$. For π incidence, the observed difference intensities are significantly different, as one would expect, as there are additional pure magnetic dipole magnetic contributions. First, $\Delta I/2I$ is much larger compared to that collected with σ polarization. This is in part due to the fact that charge scattering, which goes directly in the denominator of $\Delta I/2I$, is strongly suppressed by the polarization correction factor of $(\cos 2\theta)^2 \approx 0.011$ for the $2\theta \approx 96.1°$ of the (0-80) reflection with θ being the Bragg angle. In addition, scattering from magnetic dipole moments is possibly contributing in this channel, which leads to additional contributions, mainly occurring at the main edge. The corresponding azimuthal-angle dependence of the Friedel pair reflection is shown in Fig. 5. Despite these additional terms, we observe next to no difference in the ψ dependence at two energies in the vicinity of the pre-edge resonance A-B displayed in Fig. 1.

IV. DISCUSSION

Before we start to describe the observations with a detailed analysis using atomiclike multipoles, we will give some visual feasibility argument for the experimental signals detected in the current experiment for various azimuthal angles. We

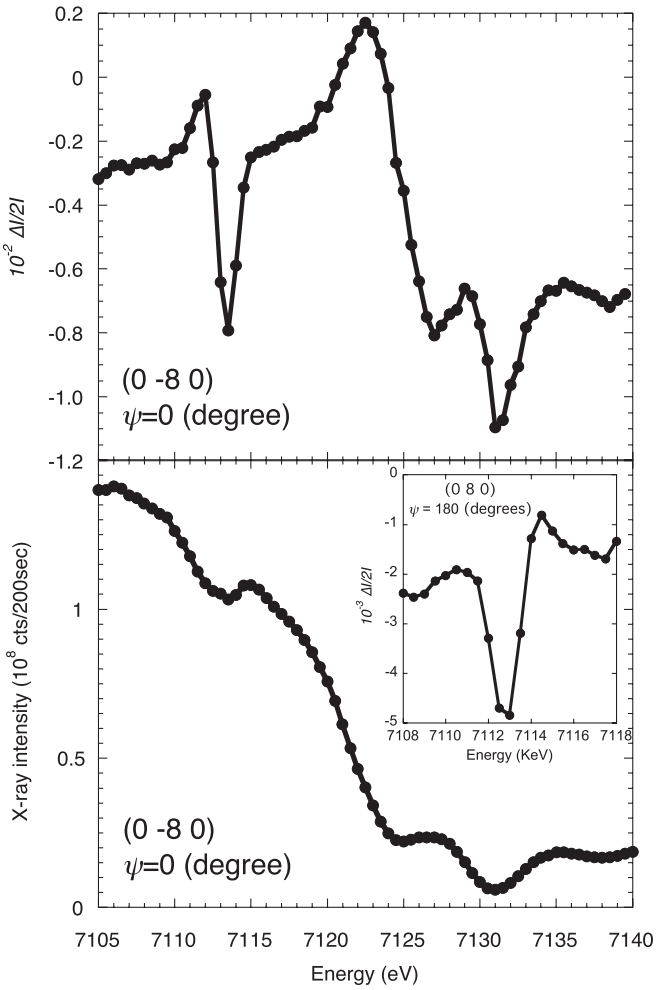

FIG. 4. Upper part: Normalized magnetic x-ray difference intensity $\Delta I/2I = (I^+ - I^-)/(I^+ + I^-)$ of the (0-80) reflection in the vicinity of the Fe K edge. Lower part: Energy dependence of the (0-80) reflection in the same energy regime. Inset: Enlarged $\Delta I/2I$ in the vicinity of the Fe K pre-edge; these data are also shown in the bottom panel of Fig. 3. All data are taken at 100 K and with π incidence x-ray polarization.

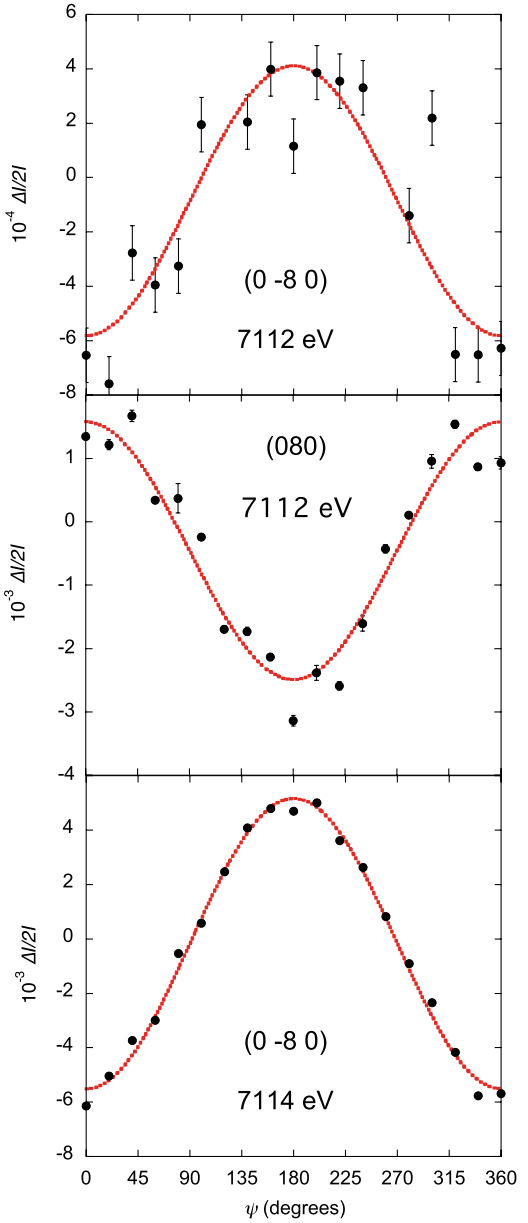

FIG. 5. (Color online) Azimuthal-angle dependence of $\Delta I/2I$ for the Friedel pair of reflections (0-80) (top panel), (080) (middle panel) at 7112 eV and 100 K with π incident radiation. The lowest panel shows the intensity of the (0-80) reflection at slightly elevated energy (7114 eV).

assume only that the result of any measurement is invariant with respect to reflection in a mirror plane.[21] In Fig. 6 top, the diffraction geometry with linear incident beam polarization is presented. The polar vector of the sample (b axis) is shown with black and white circles while the magnetic (axial, c axis) vector is represented by a current loop perpendicular to it. Mirror reflection does not alter either vector and insisting that the diffraction intensity is invariant does not rule out an intensity change upon reversing the field. This situation corresponds to $\psi = 0°$. Bottom: for $\psi = 90°$ we see that the magnetic vector is reversed by the mirror, but not the polar vector. Reversal of the magnetic vector cannot, therefore, produce an intensity change and we can rule out such a signal. The x-ray difference intensity in Figs. 2 and 5 must therefore vanish at $\psi = 90°$.

We now base the interpretation of these experimental data on atomiclike multipoles and use the established crystal[22] and magnetic symmetry.[13,23] The model in question describes the data by Arima *et al.*[7] and has been presented in detail in Ref. 9.

In accordance with general diffraction theory, space group forbidden reflections are potentially sensitive to the magnetoelectric multipoles with antiferro-type long-range order, whereas the space group allowed reflections test ferro-type order. For considering the terms in the structure factor, in particular in the regime of the Fe pre-edge, we need to consider additional events to the electric-electric dipole ($E1$-$E1$) transition. These are mainly the mixed electric-dipole–quadrupole ($E1$-$E2$) and the quadrupole-quadrupole ($E2$-$E2$)

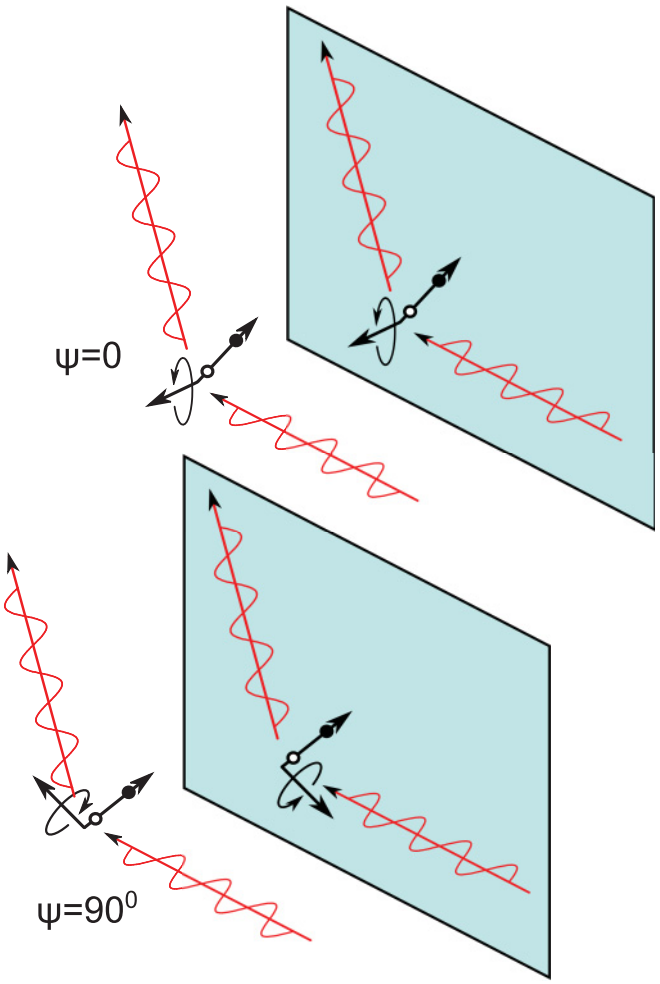

FIG. 6. (Color online) Sketch of the experiment showing the linear polarized incident and exit x rays, the polar and magnetic vector orientation for two azimuthal angles, and the crystallographic mirror plane of $GaFeO_3$.

terms and possibly the mixed electric-magnetic dipole ($E1$-$M1$), which was introduced in Ref. 9.

Based on these events, several contributions to the unit-cell structure factor, F, have to be generally considered. These are charge (Thomson) scattering (F_c), parity-even and time-odd (magnetic) multipoles in non-resonant and resonant contributions (F_m), parity-even and nonmagnetic multipoles (F_o), whose contribution is often called Templeton-Templeton or anisotropy of the tensor of susceptibility (ATS) scattering, parity-odd (polar) and nonmagnetic multipoles such as the electric-dipole moment (F_u), and magnetoelectric multipoles that violate time and space inversion (F_g). The structure factor of any reflection can be written as

$$F = F_c + F_o + F_g + F_u + F_m, \tag{1}$$

and only F_g and F_m are time odd and reverse sign on switching the polarity of the saturating applied magnetic field. Thomson scattering at space group allowed reflections under consideration is by far the largest contribution in Eq. (1) and this justifies a simplification of the expression for intensity, $I = FF^*$. Keeping pure Thomson scattering, $I_c = F_cF_c$, and contributions linear in F_c the expression for I reduces to

$$I \approx F_cF_c^* + \sum_{i=o,u,g,m} F_cF_i^* + F_iF_c^*$$

$$= I_c + \sum_{i=o,u,g,m} F_cF_i^* + F_iF_c^*. \tag{2}$$

By a field-difference method we measured $\Delta I/2I = (I^+ - I^-)/(I^+ + I^-)$, where superscripts $+$ and $-$ label parallel and antiparallel magnetization direction along the crystallographic c axis. Evidently, $\Delta I/2I$ is a linear function of contributions in Eq. (2) that change sign when the polarity of the magnetic field is switched. We obtain from Eq. (2),

$$\frac{\Delta I}{2I} \approx \frac{F_cF_m^* + F_mF_c^* + F_cF_g^* + F_cF_g^*}{I_c}. \tag{3}$$

All contributions on the right-hand side of Eq. (3) are proportional to the structure factor for Thomson scattering, which is diagonal with respect to states of polarization and vanishes for channels with rotated polarization, namely, σ-π' and π-σ'. In consequence, all structure factors that contribute in Eq. (3) are likewise diagonal with respect to states of polarization.

The energy dependence of reflections $(0k0)$ with $k = 2$ and 4 is described by interference of $E1$-$E2$ and $E1$-$M1$ with the Thomson scattering, including the sign change between the Friedel pair reflections.[9] To this successful story we must add dependences of the intensity difference (3) on primary polarization and azimuthal angle. At the K edge, magnetoelectric operators $\mathbf{G}^{\mathrm{K}}$ that appear in F_g are simple functions of the electron spin $\mathbf{S}$ and position $\mathbf{R}$ for the $E1$-$M1$ event, with orbital angular momentum $\mathbf{L}$ suitably replacing $\mathbf{S}$ in an $E1$-$E2$ event.[24] Examples of immediate interest in an $E1$-$M1$ event are $\mathbf{G}^1 \equiv$ spin anapole $= (\mathbf{S} \times \mathbf{R})$ while the quadrupole, $\mathbf{G}^2$, is created from $\mathbf{S}$ and $\mathbf{R}$ using a standard expression with diagonal component $[3z S_z - \mathbf{S}\cdot\mathbf{R}]/\sqrt{6}$. An orbital anapole $= (\mathbf{L} \times \mathbf{R}) - (\mathbf{R} \times \mathbf{L})$ and symmetrized quadrupole operator are corresponding operator equivalents in the $E1$-$E2$ event. Structure factors for magnetoelectric events are as follows.

$E1$-$M1$:

$$F_g = 8A\cos(\theta)\cos(\psi)\{\langle G_1^1\rangle' + \langle G_1^2\rangle''\}, \tag{4}$$

$E1$-$E2$:

$$F_g = 4A\cos(\theta)\cos(\psi)\left\{\frac{\sqrt{6}}{5}\langle G_1^1\rangle' - \frac{2}{\sqrt{30}}\langle G_1^2\rangle''\right\}$$

$$+ D + E\cos(2\Psi), \tag{5}$$

for the $\sigma - \sigma'$ channel, and

$E1$-$M1$:

$$F_g = 8A\cos(\theta)\cos(\psi)\{\langle G_1^1\rangle' - \langle G_1^2\rangle''\}, \tag{6}$$

$E1$-$E2$:

$$F_g = 4A\cos(3\theta)\cos(\psi)\left\{\frac{\sqrt{6}}{5}\langle G_1^1\rangle' + \frac{2}{\sqrt{30}}\langle G_1^2\rangle''\right\}$$

$$+ D' + E'\cos(2\Psi), \tag{7}$$

for $\pi - \pi'$ channel. Here, ψ is the angle of rotation of the crystal about the Bragg wave vector $(0k0)$, and the Bragg angle satisfies $\sin\theta = k\lambda/2b$ where $b \approx 9.4$ Å and the x-ray wavelength $\lambda = (12.4/\hbar\omega)$ Å with the primary energy $\hbar\omega$ in units of keV. $\langle G_1^1\rangle'$ and $\langle G_1^2\rangle''$ are the real and imaginary parts of a magnetoelectric dipole and a magnetoelectric quadrupole, respectively, $D^{(\prime)}$ and $E^{(\prime)}$ represent contributions of higher-order magnetoelectric multipole terms, and A is a complex phase factor solely determined by the positions of the Fe atoms.[9] The observed azimuthal-angle dependence of $\Delta I/2I$ is very accurately described by a pure $\cos(\psi)$ function, indicating that the D and E terms are negligible. In contrast, for the $\pi - \pi'$ channel an additional constant has to be added (subtracted) for an accurate description, but E' remains neglible. The calculated intensities are compared with experiments in Figs. 2 and 5.

We now address the energy dependence of $\Delta I/2I$. For that we exploit an important feature of the chosen reflections with $k = \pm 8$: Numerical values of F_c, considering only the atomic positions of $(0k = \pm 80)$, are real to a very good approximation and we can safely take $F_c^* \approx F_c$. This implies that it is sufficient to consider only the real part of the magnetic structure factors. As the phase factor A contributing to Eqs. (4)–(7) is for $k = \pm 8$ also dominated by the real part, we can consider only the real part of the resonance to a good approximation. The resonance of the pre-edge is well described by a simple damped harmonic oscillator function, with a real part $(E - \Delta)/[(E - \Delta)^2 + (\Gamma/2)^2]$ where Δ and Γ are the energy and width of the resonance. A single magnetoelectric resonance of this form describes nicely the energy shape of the pre-edge magnetization difference, $\Delta I/2I$, after adding a nonresonant magnetic background (see Fig. 1). Adding a second resonance does not significantly improve the agreement with the data shown in Fig. 1. A background contribution caused by nonresonant magnetic diffraction, as described by de Bergevin and Brunel,[25] would also be described by a $\cos(\psi)$ function as for the resonant term. Such a nonresonant magnetic contribution would contribute to the amplitude of the azimuthal-angle dependence. This is consistent with the data for the σ channel (Figs. 2 and 3) but not with the π-π' channel, Fig. 5, where an offset is also required in the description of the azimuthal-angle dependence. (Note that data for $\Delta I/2I$ in the π channel have a much better signal-to-noise ratio compared to data in the σ channel. This is due to the limited detector dynamic range and the strong reduction of the charge scattering in the π channel.) Whatever the origin of the nonresonant contribution is, the nonresonant magnetic scattering identified by de Bergevin and Brunel[25] is derived with a high-energy approximation,[26] which makes its validity for an application close to resonance unclear. Comparing the energy resonance of the σ and π channels for the $k = -8$ reflection shows that the shape of the energy resonance is the same. This again is consistent with the description of a single $E1$-$E2$ event [Eqs. (5) and (7)]. Though there is a sign change of the structure factor when going from σ and π ($\cos\theta > 0$ goes to $\cos3\theta < 0$), also the polarization factor of the charge scattering changes sign ($\cos2\theta < 0$) and therefore the signal, which is proportional to the interference of both, does not change sign. Consequently, the shape in energy also remains the same.

Difference spectra at the main edge also merit discussion. At these energies $\Delta I/2I$ is expected to be dominated by dipole transitions. For the σ channel, a candidate would be the $E1$-$M1$ event, as parity-even magnetic resonant scattering is absent in this channel. Magnetoelectric dipole and quadrupole contribute to scattering dictated by Fe $4p$ states, very similar to the contribution for the pre-edge. However, contributions of the $E1$-$E2$ event cannot be completely ruled out. For the π channel there will be an additional $E1$-$E1$ transition of pure magnetic origin contributing, which might be significantly larger than any $E1$-$M1$ contribution, because the relevant dipole $\langle T_0^1\rangle$ term at the K edge is proportional to the Fe $4p$-orbital magnetization. The structure factor of the pure magnetic dipole moment contribution is

$$F_m = \frac{i}{\sqrt{2}} B \sin(2\theta)\cos(\psi)\langle T_0^1\rangle, \tag{8}$$

where B is a complex phase factor given only by the Fe positions, and its real and imaginary parts satisfy $B'' \approx 3B'$. Due to the dominance of the real part in F_c, again only the real part of F_m contributes. The energy dependence of the magnetic contribution has again the shape of $(E - \Delta)/[(E - \Delta)^2 + (\Gamma/2)^2]$ as for the pre-edge, but now with the lifetime width Γ of the K edge, which is significantly larger than that of the higher-order components occurring at the pre-edge. Again this is qualitatively consistent with the observation, though an additional sharper feature is observed at approximately 7131 eV. A description of the precise energy dependence of the magnetic dipole contribution has to include the magnetic density of $4p$ states in the presence of a core hole, which goes beyond a damped harmonic oscillator function for the energy dependence considered here. A more elaborate description would also require the inclusion of the regular energy dependence of the anomalous charge scattering to F_c, which is not necessarily negligible at the Fe main K edge for the probed reflections. The presented energy-dependent reflection intensities collected in the π channel could be used to be compared with first principle calculations, such as those presented in Ref. 18. In particular, the much richer spectral shapes contain significantly more physical information compared to those obtained with σ incident radiation. This could lead to more testing and quantitative exploration of more quantitatively magnetic and magnetoelectric signals in magnetoelectric materials.

V. CONCLUSIONS

We present resonant x-ray diffraction data collected in the vicinity of the K edge of Fe for charge allowed reflections of $GaFeO_3$ at low temperatures in the ferrimagnetic phase. By using a magnetization difference method, we are able to extract magnetic and magnetoelectric signals, which are interpreted in terms of an atomiclike model. The observed magnetization difference intensities in the pre-edge regime can be understood in terms of a combination of the toroidal moment and a magnetoelectric quadrupole component of Fe $3d$ electrons. The interpretation of the magnetic difference intensity at the main edge depends on the incident light polarization. Whereas the signal for σ incidence might reflect the magnetoelectric multipoles from the Fe $4p$ states, the π

incidence signal is much larger and clearly dominated by the ferromagnetic moment induced in the Fe $4p$ shell, pointing along the crystallographic c axis. The observed nonresonant magnetic scattering remains a challenge to be understood. It has to await a clarification of the magnetic x-ray scattering formalism for "nonresonant" magnetic x-ray scattering beyond the high-energy approximation of de Bergevin and Brunel. The presented x-ray data support the occurrence of atomiclike toroidal moments and magnetoelectric quadrupoles and further provide data to be challenged by first-principle calculations, which will help clarify the role of these multipoles in magnetic systems without inversion symmetry.

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[1] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature **429**, 392 (2004).

[2] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature **426**, 55 (2003).

[3] D. Khomskii, Physics **2**, 30 (2009).

[4] Y. Bodenthin, U. Staub, M. García-Fernández, M. Janoschek, J. Schlappa, E. I. Golovenchits, V. A. Sanina, and S. G. Lushnikov, Phys. Rev. Lett. **100**, 027201 (2008).

[5] Y. Yamasaki, H. Sagayama, T. Goto, M. Matsuura, K. Hirota, T. Arima, and Y. Tokura, Phys. Rev. Lett. **98**, 147204 (2007).

[6] V. Scagnoli, U. Staub, Y. Bodenthin, R. A. De Souza, M. García-Fernández, M. Garganourakis, A. T. Boothroyd, D. Prabhakaran, and S. W. Lovesey, Science **332**, 696 (2011).

[7] T. Arima, J. H. Jung, M. Matsubara, M. Kubota, J. P. He, Y. Kaneko, and Y. Tokura, J. Phys. Soc. Jpn. **74**, 1419 (2005).

[8] S. W. Lovesey, J. Fernández-Rodríguez, J. A. Blanco, D. S. Sivia, K. S. Knight, and L. Paolasini, Phys. Rev. B **75**, 014409 (2007).

[9] S. W. Lovesey, K. S. Knight, and E. Balcar, J. Phys.: Condens. Matter **19**, 376205 (2007).

[10] V. Scagnoli and S. W. Lovesey, Phys. Rev. B **79**, 035111 (2009).

[11] U. Staub, Y. Bodenthin, C. Piamonteze, M. García-Fernández, V. Scagnoli, M. Garganourakis, S. Koohpayeh, D. Fort, and S. W. Lovesey, Phys. Rev. B **80**, 140410(R) (2009).

[12] U. Staub, Y. Bodenthin, C. Piamonteze, S. P. Collins, S. Koohpayeh, D. Fort, and S. W. Lovesey, Phys. Rev. B **82**, 104411 (2010).

[13] T. Arima, D. Higashiyama, Y. Kaneko, J. P. He, T. Goto, S. Miyasaka, T. Kimura, K. Oikawa, T. Kamiyama, R. Kumai, and Y. Tokura, Phys. Rev. B **70**, 064426 (2004).

[14] J. H. Jung, M. Matsubara, T. Arima, J. P. He, Y. Kaneko, and Y. Tokura, Phys. Rev. Lett. **93**, 037403 (2004).

[15] M. Kubota, T. Arima, Y. Kaneko, J. P. He, X. Z. Yu, and Y. Tokura, Phys. Rev. Lett. **92**, 137401 (2004).

[16] U. Staub, Y. Bodenthin, M. García-Fernández, R. A. de Souza, M. Garganourakis, E. I. Golovenchits, V. A. Sanina, and S. G. Luschnikov, Phys. Rev. B **81**, 144401 (2010).

[17] J. Y. Kim, T. Y. Koo, and J. H. Park, Phys. Rev. Lett. **96**, 047205 (2006).

[18] S. Di Matteo and Y. Joly, Phys. Rev. B **74**, 014403 (2006).

[19] Y. Joly, O. Bunau, J. E. Lorenzo, R. M. Galera, S. Grenier, and B. Thompson, J. Phys.: Conf. Ser. **190**, 012007 (2009).

[20] [http://www.diamond.ac.uk/Home/Beamlines/I16/status.html].

[21] S. P. Collins, S. W. Lovesey, and E. Balcar, J. Phys.: Condens. Matter **19**, 213201 (2007).

[22] E. A. Wood, Acta Crystallogr. **13**, 682 (1960).

[23] R. B. Frankel, N. A. Blume, S. Foner, A. J. Freemann, and M. Schieber, Phys. Rev. Lett. **15**, 958 (1965).

[24] S. W. Lovesey and E. Balcar, Phys. Scr. **81**, 065703 (2010).

[25] F. de Bergevin and M. Brunel, Acta Crystallogr. A **37**, 314 (1981).

[26] S. W. Lovesey, Rep. Prog. Phys. **56**, 257 (1993).