Exchange-striction associated with the elliptical proper helical magnetic structure in the ferroelectric phase of CuFe$_{1-y}$Ga$_y$O$_2$

N Terada$^{1,3,4}$, T Nakajima$^2$, S Mitsuda$^2$, M Matsuda$^3$, K Kakurai$^3$, Y Tanaka$^4$ and H Kitazawa$^1$

$^1$National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, 305-0047, Japan
$^2$Department of Physics, Tokyo University of Science, Tokyo 162-8601, Japan
$^3$Japan Atomic Energy Agency, Tokai, Ibaraki, 319-1195, Japan
$^4$RIKEN SPring-8 Center, Harima Institute, Sayo, Hyogo 679-5148, Japan

E-mail: terada.noriki@nims.go.jp

Abstract. Recently, the detail magnetic structure in the ferroelectric phase of CuFe$_{1-y}$Ga$_y$O$_2$ has been determined to be the proper helical structure with the ellipticity of $\sim 0.9$ by the comprehensive neutron diffraction study.[Nakajima et al. Phys. Rev. B 79 214423 (2009)] In the present study, we have investigated the lattice modulation associated with the elliptical magnetic structure, using the resonant X-ray diffraction measurements on CuFe$_{0.965}$Ga$_{0.035}$O$_2$. We observed the superlattice reflection indexed as (0 1 + 2$q_{m}$ 0), where $q_{m}$ is the wave number of the magnetic modulation. The energy spectrum near the Fe-K absorption edge for the (0 1 + 2$q_{m}$ 0) intensity conforms with that for the fundamental (0 2 0) intensity within experimental accuracy, suggesting that the superlattice modulation is at least associated with displacements of the Fe ions. We discuss the origin of the superlattice modulation with the exchange striction model.

1. Introduction
In recent years, magneto-electric multiferroic materials have attracted much attention with the aim of clarifying the novel microscopic coupling between spin and electric dipole moment.[1] The theoretical study has presented three possible mechanisms regarding coupling between spin and electric dipole moment: (i) exchange-striction, (ii) spin-current[2] and (iii) $d$-$p$ hybridization mechanisms.[3] In a majority of multiferroic materials with a non-collinear magnetic ordering and a ferroelectric polarization, the second mechanism has succeeded in explaining the appearance of their ferroelectricity. In CuFeO$_2$, however, the ferroelectricity can be explained with the third mechanism, which was argued by Arima.[4] He also predicted that the electric dipole moments are modulated with twice larger wave number, 2$q_{m}$, than the magnetic one, $q_{m}$ in the ferroelectric phase of CuFeO$_2$. Although the superlattice reflection with 2$q_{m}$ was observed in the previous non-resonant X-ray diffraction measurements,[5] the origin of the superlattice modulation has not been revealed so far.

CuFeO$_2$ shows both magnetic field-induced[6] and nonmagnetic (Al or Ga) impurity-substitution-induced[7, 8] ferroelectric phase transitions. The magnetic phase diagram of CuFe$_{1−y}$Ga$_y$O$_2$ is shown in figure 1.[9] Recently, Nakajima et al. have demonstrated the
Figure 1. (a) Magnetic phase diagram of CuFe$_{1-y}$Ga$_y$O$_2$. The data were taken from Ref. [9]. (b) Elliptical proper helical magnetic structure in the FEIC phase with the monoclinic basis, $a_m$, $b_m$ and $c_m$. Cartesian coordinate, $x$, $y$ and $z$, is also drawn. The $x$ and $y$ axes are parallel to $a_m$ and $b_m$ axes, respectively. The $z$ axis is perpendicular to the $a_m b_m$ plane.

comprehensive study using both the spherical neutron polarimetry and the unpolarized neutron diffraction with the four-circle diffractometer, and have determined the elliptical proper helical magnetic structure with the ellipticity of $\sim 0.9$ in CuFe$_{0.965}$Ga$_{0.035}$O$_2$.[10] There are two possible mechanisms regarding the $2q_m$ modulation, which are the exchange-striction and the $d - p$ hybridization mechanisms. In the present study, in order to investigate the origin of the $2q_m$ superlattice modulation in the ferroelectric phase, we have performed the resonant X-ray diffraction (RXD) experiments on the single crystal of CuFe$_{0.965}$Ga$_{0.035}$O$_2$.

2. Experimental detail
The single crystal of CuFe$_{0.965}$Ga$_{0.035}$O$_2$, which was prepared by the floating zone technique,[11] was cut into a disk with a thickness of 2 mm and subsequently polished to remove the surface roughness. The surface is perpendicular to the monoclinic $b$ axis. In this paper, we use the monoclinic notation with the unique axis $b$ and the cell choice 1 in the space group $C2/m$. While the lattice parameters were not refined in CuFe$_{0.965}$Ga$_{0.035}$O$_2$, those of CuFeO$_2$ were
reported in the previous paper.[12] The monoclinic unit cell is illustrated in figure 1(b). The RXD experiments were carried out with a standard four-circle diffractometer in BL29XU at SPring-8. The cut crystal was mounted in a liquid 4He refrigerator that can cool a sample down to 3 K. The incident X-ray beam had almost perfect horizontal polarization and its energy was tuned to near the Fe-K absorption edge. \((E \approx 7.112\text{ keV})\) The diffracted X-rays were analyzed using the 006 reflection of a pyrolytic graphite crystal.

3. Experimental results
As shown in figure 2(a), the energy dependence of the superlattice reflection at \((0 1 + 2q_m 0)\) conforms with that of the fundamental 020 reflection, within the experimental accuracy. No resonant enhancement that corresponds to the \(2q_m\) modulation of the \(d-p\) hybridization was observed near the Fe-K edge. The energy dependence of the structure factor of the fundamental 020 reflection near the Fe-K absorption edge can be written as

\[
F_{020} \propto f_{Fe}' + if_{Fe}'' + C
\]  

where \(f_{Fe}'\) and \(f_{Fe}''\) are real and imaginary parts of anomalous scattering factor of Fe atom, respectively. \(C\) is independent of energy. Note that the energy spectrum near the edge depends only on the anomalous scattering factors of Fe atom. Considering that the spectrum of the fundamental reflection conforms with that of the superlattice reflection at \((0 1 + 2q_m 0)\), we thus conclude that the superlattice reflection at least originates from atomic displacements of Fe atoms.

The spectra of the superlattice reflection at \((0 1 + 2q_m 0)\) with \(\pi - \pi'\) and \(\pi - \sigma'\) channels are shown in figure 2(b). While the spectrum of intensity in \(\pi - \pi'\) channel is identical to the case without analyzer (figure 2(a)), the intensity in \(\pi - \sigma'\) channel is zero in every energy. These results infer that the superlattice reflection originates from the charge scattering and support our conclusion mentioned above.

![Figure 2](image_url)

**Figure 2.** Energy dependence of the intensity of the fundamental reflection at (020) and the superlattice reflection at \((0 1 + 2q_m 0)\), which are represented by closed and open symbols, respectively. As for the superlattice reflection, the diffracted X-ray beams were not analyzed in (a) and analyzed into \(\pi - \pi'\) and \(\pi - \sigma'\) channels in (b). The fluorescence spectrum is shown in the inset on (a).
4. Discussion
As mentioned above, we concluded that the superlattice reflection with 2q_m wave number at least originates from the atomic displacement of Fe atom. In the present work, we focus upon discussing whether the displacement is explained by the exchange-striction mechanism.

4.1. Exchange-striction model
We calculate atomic displacement through the exchange-striction for Fe atoms, associated with the elliptical proper helical magnetic ordering, in the ferroelectric phase of CuFe_{1-y}Ga_yO_2. Here, we consider the exchange-striction for two Fe sites, Fe1 and Fe2, which is illustrated in figure 3. Assuming that only nearest neighbor exchange interactions contribute the exchange-striction, the atomic displacement for Fe1(Fe2) is proportional to sum of the magnetoelastic energy between spin on Fe1(Fe2) site and its nearest neighbor spins. The general form is written as

\[ L_{Fe_n} = \sum_{i}^{NN} \alpha_i (r_n - r_i) (S_n \cdot S_i), \]  

(2)

where \( \alpha_i \) is magnetoelastic constant. In the present calculation, \( \alpha \) is assumed to be identical for the six nearest neighbor exchange bonds.

When we define the Cartesian coordinate illustrated in figure 1(b), the spin components[10] are written as

\[
\begin{align*}
S^x_{l,d_i} &= \mu_x \cos[Q \cdot (l + d_i) - \phi_i] \\
S^y_{l,d_i} &= 0 \\
S^z_{l,d_i} &= \mu_z \sin[Q \cdot (l + d_i) - \phi_i].
\end{align*}
\]

(3)

\( Q \) is the magnetic propagation vector of \( 0 \) to \( \frac{1}{2} \). \( d_i \) denotes the fractional coordinates represented by the monoclinic basis described in figure 1(b). \( \phi_i \) is the relative phase shift at the \( d_i, \phi_{1,3,4,7,8} = 0 \) and \( \phi_{2,5,6,9,10} = \delta \).

Using the eqs. (2) and (3), we calculate the atomic displacements along the b axis for Fe1 and Fe2,

\[
\begin{align*}
L^b_{Fe1} &= A(\mu_x^2 + \mu_z^2) \sin(\delta) + C(\mu_z^2 - \mu_x^2) \sin(2\pi(2q_m)y) \\
L^b_{Fe2} &= -A(\mu_x^2 + \mu_z^2) \sin(\delta) + C(\mu_z^2 - \mu_x^2) \sin(2\pi(2q_m)y + \Delta),
\end{align*}
\]

(4) (5)

Figure 3. (a) Schematic drawing of the nearest neighbor Fe ions for Fe1 and Fe2 sites in the ab plane. (b) Illustration of the displacement along the b direction. The phase difference between the lattice modulations through Fe1 and Fe2 sites is represented by \( \Delta \). Note that the vertical axis denotes the displacements along the b axis.
where $A = \sin(\pi q_m)$, $B = \sin(2\pi q_m)$ and $C = \sqrt{A^2 + B^2 + 2AB \cos(\delta)}$. $\Delta$ is the phase difference for the lattice modulation,

$$
\Delta = 2 \arctan \left( \frac{B \sin(\delta)}{A + B \cos(\delta)} \right).
$$

The first terms in eqs. (4) and (5) are constants in space, which reflects uniform displacements. These uniform terms are identical in their absolute value and their signs are opposite. Therefore, the first terms give antiferroic displacements along the $b$ axis on Fe1 and Fe2 sites when $\delta$ is finite. This calculation is consistent with the observation of the 0 $k$ 0 superlattice reflection with $k = $ even, which was reported in the previous X-ray diffraction measurements.[5]

On the other hand, in the exchange-striction model above mentioned, the ratio of the intensity $q_m$ values, $I(0 4 + 2q_m 0) / I(0 3 + 2q_m 0)$, are identical in their absolute value and their signs are opposite. Therefore, the first terms in eqs. (4) and (5) are constants in space, which reflects uniform displacements.

The second terms correspond to the displacements modulated with $2q_m$. These terms are proportional to $(\mu_x^2 - \mu_z^2)$ that is not zero; because, the ellipticity was determined to be $\mu_x / \mu_z \approx 0.9$ in the recent neutron diffraction study.[10] Note that the oscillation terms for Fe1 and Fe2 sites are different in their initial phase by the phase difference $\Delta$. When the values $q_m = 0.406$ and $\delta = q_m \pi$, which were determined in the neutron diffraction study,[10] are substituted in the eq. (6), we obtain $\Delta = 0.292\pi$. The structure factor of the oscillation terms can be written as

$$
F_{2q_m} \propto (\mu_x^2 - \mu_z^2) \sum_y \left[ \sin(2\pi(2q_m)y) + e^{i\pi k} \sin(2\pi(2q_m)y + \Delta) \right] e^{2\pi i k y}, \quad (7)
$$

where $k$ is $y$ component of the index. Writing a delta function as $\delta(\cdots)$ at the moment, eq. (7) is rewritten as

$$
(\mu_x^2 - \mu_z^2) \left[ \{1 + e^{i(\pi k - \Delta)}\} \sum \delta(k + 2q_m - \tau) - \{1 + e^{i(\pi k + \Delta)}\} \sum \delta(k - 2q_m - \tau) \right]. \quad (8)
$$

Consequently, the satellite reflections indexed as $(0 k \pm 2q_m 0)$ are predicted in the present calculation. These results are in agreement with the observation of the superlattice reflection at $(0 1 + 2q_m 0)$, qualitatively.

### 4.2. Comparison between experimental results and the calculation

We discuss the oscillation terms calculated above, quantitatively. In the previous non-resonant X-ray diffraction measurements on CuFeO$_2$,[13] the reflections at $(0 4 - 2q_m 0)$ and $(0 3 + 2q_m 0)$ are observed in the ferroelectric phase. The intensity ratio between the two reflections observed in the experiments[13] is

$$
I(0 3 + 2q_m 0) / I(0 4 - 2q_m 0) \approx 10^2. \quad (9)
$$

On the other hand, in the exchange-striction model above mentioned, the ratio of the intensity in the case $k$ is even or odd is derived using eq. (8) with $\Delta = 0.292\pi$,

$$
\left| F_{2q_m}^{\text{even}} \right|^2 / \left| F_{2q_m}^{\text{odd}} \right|^2 \approx \left| 1 - e^{i\Delta} \right|^2 \left| 1 + e^{i\Delta} \right|^2 \approx 1 / 4. \quad (10)
$$

This calculated value is not coincident with the experimental value at all. Although the observation of the reflections indexed as $(0 k_{\text{even}} \pm 2q_m 0)$ with $(0 k_{\text{odd}} \pm 2q_m 0)$ can be qualitatively explained by the exchange-striction model, the intensity ratio between them cannot be quantitatively done at all. The discrepancy between the experimental facts and the model calculation might be caused by the oversimplification of the exchange-striction model.
In this calculation, the magnetoelastic constants $\alpha$ in eq. (2) are assumed to be identical for the six nearest neighbor bonds, though these bonds are not equivalent owing to the symmetry lowering from rhombohedral to monoclinic below the Néel temperature. In fact, when $\alpha$ of the bonds along the $b$ axis is much larger than the others, the ratio in eq. (10) increases about 10. This explains the tendency of $I(0 3 + 2q_{m} 0) > I(0 4 - 2q_{m} 0)$ observed experimentally.

We should also mention the temperature dependence of the ellipticity that increases with increasing temperature in the ferroelectric phase, which was reported in the recent neutron diffraction study.[10] The intensity of the $2q_{m}$ reflection is also enhanced with increasing temperature near the phase transition temperature, which is reported in the previous non-resonant X-ray diffraction study.[5] These experimental facts support the exchange-striction mechanism.

5. Summary
We have investigated the lattice modulation associated with the elliptical magnetic structure that has been determined in the recent neutron diffraction experiments,[10] using the resonant X-ray diffraction measurements on CuFe$_{0.965}$Ga$_{0.035}$O$_{2}$. We observed the superlattice reflection indexed as $(0 1 + 2q_{m} 0)$, where $q_{m}$ is the wave number of the magnetic modulation. The energy spectrum near the Fe-K absorption edge for the $(0 1 + 2q_{m} 0)$ intensity conforms with that for the fundamental $(0 2 0)$ intensity within experimental accuracy, suggesting that the superlattice modulation is at least associated with displacements of the Fe ions. We also calculated the lattice modulation associated with the elliptical proper helical magnetic structure, using the exchange-striction model involving the only nearest neighbor exchange interactions. The exchange-striction model succeeds in explaining the observation of the reflections indexed as $(0 k_{\text{even}} \pm 2q_{m} 0)$ with $(0 k_{\text{odd}} \pm 2q_{m} 0)$ qualitatively. However, the intensity ratio between these two reflections cannot be explained quantitatively, which might be caused by anisotropic magnetoelastic constants.

Acknowledgments
This work is partly supported by Grants-in-Aid for Scientific Research “Young Scientists (B), No. 20740209” and “Scientific Research (A), No. 21244049” from the Japan Society for the Promotion of Science. This work is also supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 19052004).

References
[1] Cheong S-W and Mostovoy M 2007 Nature Mater. 6 13
[2] Katsura H, Nagaosa N and Balatsky A V 2005 Phys. Rev. Lett. 95 057205
[3] Jia C, Onoda S, Nagaosa N and Han J H 2007 Phys. Rev. B 76 144424
[4] Arima T 2007 J. Phys. Soc. Jpn. 76 073702
[5] Nakajima T, Mitsuda S, Inami T, Terada N, Ohsumi H, Prokes K and Podlesnyak A 2008 Phys. Rev. B 78 024106
[6] Kimura T, Lashley J C and Ramirez A P 2006 Phys. Rev. B 73 220401(R)
[7] Seki S, Yamasaki Y, Shiomi Y, Iuchi S, Onose Y and Tokura Y 2007 Phys. Rev. B 75 100403(R)
[8] Terada N, Nakajima T, Mitsuda S, Kitazawa H, Kaneko K and Metoki N 2008 Phys. Rev. B 78 014101
[9] Terada N, Nakajima T, Mitsuda S and Kitazawa H 2009 J. Phys. Conference Series 145 012071
[10] Nakajima T, Mitsuda S, Takahashi K, Yamano M, Masuda K, Yamazaki H, Prokes K, Kiefer K, Gerischer S, Terada N, Kitazawa H, Matsuda M, Kakurai K, Kimura H, Noda Y, Soda M, Matsuura M and Hirota K 2009 Phys. Rev. B 79 214423
[11] Zhao T R, Hasegawa M and Takei H 1996 J. Cryst. Growth 166 408
[12] Ye F, Ren Y, Huang Q, Fernandez-Baca J A, Dai P, Lynn J W and Kimura T 2006 Phys. Rev. B 73, 220404(R)
[13] Terada N, Mitsuda S, Tanaka Y, Tabata Y, Katsumata K and Kikkawa A 2008 J. Phys. Soc. Jpn. 77 054701