Circularly polarized soft x-ray diffraction study of helical magnetism in hexaferrite

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Magnetic spiral structures can exhibit ferroelectric moments as recently demonstrated in various multiferroic materials. In such cases the helicity of the magnetic spiral is directly correlated with the direction of the ferroelectric moment and measurement of the helicity of magnetic structures is of current interest. Soft x-ray resonant diffraction is particularly advantageous because it combines element selectivity with a large magnetic cross-section. We calculate the polarization dependence of the resonant magnetic x-ray cross-section and demonstrate there is a direct correlation between the diffracted radiation and the helicity of the magnetic spiral.

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Magnetic spiral structures can exhibit ferroelectric moments as recently demonstrated in various multiferroic materials. In such cases the helicity of the magnetic spiral is directly correlated with the direction of the ferroelectric moment and measurement of the helicity of magnetic structures is of current interest. Soft x-ray resonant diffraction is particularly advantageous because it combines element selectivity with a large magnetic cross-section. We calculate the polarization dependence of the resonant magnetic x-ray cross-section and demonstrate there is a direct correlation between the diffracted radiation and the helicity of the magnetic spiral.

We demonstrate that XRD is well suited to study magnetoelastic coupling in multiferroic materials that exhibit magnetic spiral components.

The helical magnetic structure of Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$ hexaferrite has been studied with neutron scattering and polarized x-ray diffraction and is characterized by (0 0 1°) satellites with $l^2 = 3n^2 ± 3$. The competition among superexchange interactions leads to a distorted helimagnetic structure consisting of large and small ferrimagnetic bunches with moments aligned in the $ab$ plane and modulation wave vector (0 0 $\tau$). Electric polarization arises under applied magnetic field in the intermediate-III magnetic phase, characterized by $\tau = 0.5$.

Hexaferrite single crystals were grown in a manner similar to that given by Momozawa et al. Reactants were mixed in the molar ratio 4.92% BaCO$_3$, 14.77% SrCO$_3$, 19.69% ZnO, 53.61% Fe$_2$O$_3$, and 7.01% Na$_2$CO$_3$ flux and heated in a Pt crucible to 1420 °C at a rate of 20 °C min and left there for 20 h. Rapid temperature cycling was employed to employ impurity crystals followed by slow cooling (0.2 °C/h) between 1185 and 1155 °C to improve crystal size.

Elemental analysis with inductively coupled plasma atomic emission spectroscopy gave a stoichiometry of Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$, with small variations in Ba/Sr ratio depending on the single crystal. Magnetization measurements were performed with a Quantum Design 7T MPMS at the magnetics laboratory at the University of Western Australia. The single crystals exhibited consecutive magnetization steps as function of applied magnetic field in the $ab$ plane, similar to results reported earlier. Single-crystal neutron diffraction was performed at the Wombat diffractometer at OPAL with $\lambda = 2.955$ Å and showed temperature-dependent incommensurate $\tau$ for $B = 0$ T, $\tau = 0.5$ for $0.5 \leq B \leq 2.0$ T, and $\tau = 1$ for $B \geq 2.25$ T (at $T = 100$ K). Soft x-ray resonant diffraction was performed at the RESOX beam station of the SIM beamline at the Swiss Light Source of the Paul Scherrer Institut.

In this Brief Report we calculate the polarization dependence of the RXD cross-section and deduce the domain population of the magnetic spiral structure in hexaferrite using variably polarized incident radiation at the Fe $L_3$ edge ($\lambda = 17.45$ Å). We demonstrate that XRD is well suited to study magnetoelastic coupling in multiferroic materials that exhibit magnetic spiral components.

Correlation between the RXD intensity and the helicity of the magnetic spiral has been demonstrated by imaging of the magnetic spiral in holmium.

In the case of transition metals, the electronic emission spectroscopy gave a stoichiometry of Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$, with small variations in Ba/Sr ratio depending on the single crystal. Magnetization measurements were performed with a Quantum Design 7T MPMS at the magnetics laboratory at the University of Western Australia. The single crystals exhibited consecutive magnetization steps as function of applied magnetic field in the $ab$ plane, similar to results reported earlier. Single-crystal neutron diffraction was performed at the Wombat diffractometer at OPAL with $\lambda = 2.955$ Å and showed temperature-dependent incommensurate $\tau$ for $B = 0$ T, $\tau = 0.5$ for $0.5 \leq B \leq 2.0$ T, and $\tau = 1$ for $B \geq 2.25$ T (at $T = 100$ K). Soft x-ray resonant diffraction was performed at the RESOX beam station of the SIM beamline at the Swiss Light Source of the Paul Scherrer Institut.

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in the scattering plane and the \(a\) axis perpendicular to the scattering plane (see Fig. 1) and its temperature was regulated between 15 and 325 K.

X-ray diffraction from magnetic spiral structures gives rise to satellite reflections, which have polarization-dependent magnetic scattering cross-sections. The intensity from magnetic moments is proportional to \((\hbar \omega/mc^2)^2\) and is generally weak. However, this is enhanced by orders of magnitude when the x-ray energy is tuned to an absorption edge generally vanishing but can be nonzero as demonstrated for the case of the enantiomorphic screw axis in quartz.  

We approximate the magnetic structure of hexaferrite with a single magnetic moment that rotates either clockwise (positive helicity \(S^+\)) or anticlockwise (negative helicity \(S^-\)) for consecutive atoms along the \(c\) axis. For a basal plane magnetic spiral with modulation wave vector (0 0 \(\tau\)) the direction for \(S^+\) and \(S^-\) equals \(\vec{z}_j^+ = \vec{u}_1 \cos(\tau \vec{r}_j) \pm \vec{u}_2 \sin(\tau \vec{r}_j)\). The unit vectors \(\vec{u}_1\), \(\vec{u}_2\), and \(\vec{u}_3\) define the coordinate system with respect to the diffraction plane. \(\vec{u}_1\) is parallel to \(\vec{k}' + \vec{k}\), \(\vec{u}_2\) is perpendicular to the scattering plane, and \(\vec{u}_3\) is parallel to \(\vec{k}' - \vec{k}\) (see Fig. 1). In this experiment the \(c\) axis of hexaferrite is aligned along \(\vec{u}_3\). The cross terms of polarization \(\vec{e}' \times \vec{e}\) in Eq. (1) equal \(\vec{\alpha}' \times \vec{\alpha} = 0\), \(\vec{\alpha}' \times \vec{\pi} = -\vec{k}\), \(\vec{\pi}' \times \vec{\alpha} = -\vec{k}'\), and \(\vec{\pi}' \times \vec{\pi} = \vec{k}' \times \vec{k}\). Consequently, the polarization-dependent magnetic structure factors are

\[
M_{\alpha'\alpha} = 0, 
\]

\[
M_{\alpha'\pi} = -\frac{3}{4\epsilon_0} \sum_j \left( \vec{k}' \cdot \vec{z}_j^+ \right) \left[ F_{11} - F_{1\perp} \right] \exp(i \vec{q} \cdot \vec{r}_j), 
\]

\[
M_{\pi'\pi} = -\frac{3}{4\epsilon_0} \sum_j \left( \vec{k} \times \vec{\hat{k}} \right) \left[ F_{11} - F_{1\perp} \right] \exp(i \vec{q} \cdot \vec{r}_j), 
\]

\[
M_{\pi'\sigma} = -\frac{3}{4\epsilon_0} \sum_j \left( \vec{k}' \times \vec{\hat{k}} \right) \left[ F_{11} - F_{1\perp} \right] \exp(i \vec{q} \cdot \vec{r}_j). 
\]

Using \(\vec{k} = \vec{u}_1 \cos \theta + \vec{u}_2 \sin \theta\), \(\vec{k}' = \vec{u}_1 \cos \theta - \vec{u}_2 \sin \theta\), and \(\vec{\hat{k}} \times \vec{\hat{k}} = -\vec{u}_3 \sin 2 \theta\) gives for the resonant intensity of the magnetic satellites

\[
I_{\alpha, S\pm}^{\text{XRES}} \propto \cos^2 \theta [F_{11} - F_{1\perp}] \delta(\vec{q} \pm \vec{\tau}), 
\]

\[
I_{\pi, S\pm}^{\text{XRES}} \propto (\cos^2 \theta + \sin^2 2 \theta)[F_{11} - F_{1\perp}] \delta(\vec{q} \pm \vec{\tau}), 
\]

\[
I_{\pi, S\pm}^{\text{XRES}} \propto \left( \cos^2 \theta + \frac{1}{2} \sin^2 2 \theta \sin \chi \cos \theta \sin 2 \theta \right) \times [F_{11} - F_{1\perp}] \delta(\vec{q} \pm \vec{\tau}), 
\]
TABLE I. Experimental (exp.) and calculated (calc.) intensities for the magnetic satellites observed in hexaferrite using 77% of magnetic domains with $S^+$ and 23% of magnetic domains with $S^-$. A single scaling factor was used between experimental and calculated intensities.

| Incident polarization | (003$^-$) Exp. | (003$^-$) Calc. | (003$^+$) Exp. | (003$^+$) Calc. |
|-----------------------|----------------|----------------|----------------|----------------|
| RCP                   | 0.50           | 0.52           | 0.11           | 0.10           |
| LCP                   | 0.24           | 0.25           | 0.25           | 0.23           |
| $\sigma$              | 0.23           | 0.26           | 0.08           | 0.08           |
| $\pi$                 | 0.50           | 0.51           | 0.27           | 0.25           |

of the helicity of the magnetic spiral, in contrast to the diffracted intensity for circular polarization, which is distinct for $S^+$ and $S^-$. The term proportional to $\cos \theta \sin 2\theta$ is opposite in sign for the satellites at $(0 \ 0 \ 1^-)$ and $(0 \ 0 \ 1^+)$ and, for each satellite, the difference in resonant intensity for RCP and LCP incident radiation is proportional to $2\cos \theta \sin 2\theta (F_{11^-} - F_{11^+})^2$. This demonstrates a direct correlation between diffracted intensity of circularly polarized x rays and the helicity of the magnetic spiral. The deduced intensities [Eqs. (9)–(12)] are independent of rotation of the sample around the scattering factor $q$.

Figure 2 illustrates that $(0 \ 0 \ 3^-)$ is most intense for LCP and $(0 \ 0 \ 3^+)$ is most intense for RCP radiation. In contrast, linear polarization of the incident radiation does not result in such asymmetry. The diffracted intensity for $\pi$ radiation is stronger than for $\sigma$ radiation consistent with Eqs. (9) and (10). The resonant Bragg intensity as a function of incident energy for the $(003^\pm)$ satellite is distinct from that of the $(003)$ reflection and orders of magnitude stronger than the fluorescence yield (Fig. 3). Table I compares the observed and calculated intensities demonstrating good agreement, 77% exhibits a magnetic spiral with $S^+$ and 23% a magnetic

FIG. 2. (Color online) Resonant diffraction of hexaferrite at $T = 35 \text{ K}$ recorded with (a) circular- and (b) linear-polarized incident radiations at the Fe $L_3$ edge. Note the asymmetry in intensity of the two magnetic satellites neighboring the (003) reflection recorded with RCP (red crosses) and LCP (blue filled spheres). $\sigma$ (blue filled triangles) and $\pi$ (red plusses) diffractions do not distinguish between positive and negative helicities of the magnetic spiral.

$F_{\chi,S}^{\text{XRES}} \propto \left( \cos^2 \theta + \frac{1}{2} \sin^2 2\theta \pm \chi \cos \theta \sin 2\theta \right) \times [F_{11} - F_{11^-}]^2 \delta(q \pm \tau).$ (12)

The diffracted intensity for linear polarization is independent

FIG. 3. (Color online) (a) Energy dependence of the $(003^-)$ magnetic satellite (b) compared to the (003) structural reflection and (c) the fluorescence yield, recorded with $\sigma$ (solid red) and $\pi$ (dotted blue) linear polarized incident radiations. Note the scaling factors used. The spectra were recorded at $T \approx 90 \text{ K, 132 K, and 138 K}$, respectively, and are not corrected for absorption.

FIG. 4. (Color online) Wave vector of the magnetic spiral in hexaferrite as a function of temperature deduced from the resonant magnetic satellite diffraction (open symbols) and neutron diffraction (solid symbols). The difference in the magnitude of $\tau$ for XRD and ND is attributed to stoichiometry variation between the single crystals used in the experiments.
spiral with $S^*$ within the illuminated sample area of $\sim 1$ mm$^2$.

Figure 4 shows the gradual modulation of the wave vector of the magnetic spiral with increasing temperature. Variations in stoichiometry result in different $\tau$ due to modification of the superexchange interaction. The general trend is similar to that observed for Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$.19,21

RXD from the magnetic spiral is intense and on average about a factor of two smaller than the diffracted intensity at (003). This is much stronger than the nonresonant x-ray diffracted intensity reported for Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$.22 The long wavelength makes soft x-ray resonant diffraction particularly suited to study magnetic structures with large periodicity. Recently, soft x-ray diffraction studies at the Mn $L_3$ edge have measured the magnetic spin structure and order parameter in multiferroic TbMn$_2$O$_5$ demonstrating the magnetoelectric effect arises from noncollinear spin moments.29 An in situ applied electric field demonstrated significant manipulation and the excitation of commensurate magnetic order in multiferroic ErMn$_2$O$_5$.30 Very recently circularly polarized radiation at the Dy $M_5$ resonance has been used to write and read chiral domains in multiferroic DyMn$_3$.31

In summary, we present polarization-dependent resonant diffraction cross-sections for $\sigma$, $\pi$, LCP, and RCP incident radiation and determine the spiral magnetic domain population. This demonstrates the potential of using circularly polarized soft x-ray resonant diffraction for investigation of long-wavelength magnetic structures. Compared to polarized neutron studies, this method records element specific magnetic helicity and allows to differentiate between distinct magnetic ions within one material. The large diffracted intensity, limited sample size requirements, and speed of collection times are an additional advantage.

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1 T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) 426, 55 (2003).
2 K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. 97, 097203 (2006).
3 G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. 95, 087205 (2005).
4 T. Kimura, G. Lawes, and A. P. Ramirez, Phys. Rev. Lett. 94, 137201 (2005).
5 J. P. Hannon, G. T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. 61, 1245 (1988).
6 M. Blume, Phys. Rev. 130, 1670 (1963).
7 K. Siratori, J. Akimitsu, E. Kita, and M. Nishi, J. Phys. Soc. Jpn. 48, 1111 (1980).
8 Y. Yamasaki, H. Sagayama, T. Goto, M. Matsuura, K. Hirota, T. Arima, and Y. Tokura, Phys. Rev. Lett. 98, 147204 (2007).
9 S. Seki, Y. Yamasaki, M. Soda, M. Matsuura, K. Hirota, and Y. Tokura, Phys. Rev. Lett. 100, 127201 (2008).
10 T. Nakajima, S. Mitsuda, S. Kanetsuki, K. Tanaka, K. Fujii, N. Terada, M. Soda, M. Matsuura, and K. Hirota, Phys. Rev. B 77, 052401 (2008).
11 C. Sutter, G. Grübel, C. Vettier, F. de Bergevin, A. Stunault, D. Gibbs, and C. Giles, Phys. Rev. B 55, 954 (1997).
12 F. Fabrizi, H. C. Walker, L. Paolasini, F. de Bergevin, A. T. Boothroyd, D. Prabhakaran, and D. F. McMorrow, Phys. Rev. Lett. 102, 237205 (2009).
13 U. Staub, V. Scagnoli, A. M. Mulders, K. Katsumata, Z. Honda, H. Grimmer, M. Horisberger, and J. M. Tonnerre, Phys. Rev. B 71, 214421 (2005).
14 S. B. Wilkins, N. Stojic, T. A. W. Beale, N. Binggeli, C. W. M. Castleton, P. Bencok, D. Prabhakaran, A. T. Boothroyd, P. D. Hatton, and M. Altarelli, Phys. Rev. B 71, 245102 (2005).
15 J. Herrero-Martín, J. García, G. Subías, J. Blasco, M. C. Sánchez, and S. Stanescu, Phys. Rev. B 73, 224407 (2006).
16 V. Scagnoli, U. Staub, A. M. Mulders, M. Janousch, G. I. Meijer, G. Hammerl, J. M. Tonnerre, and N. Stojic, Phys. Rev. B 73, 100409(R) (2006).
17 C. Lang, D. R. Lee, D. Haskel, and G. Srajer, J. Appl. Phys. 95, 6537 (2004).
18 U. Enz, J. Appl. Phys. 32, 225 (1961).
19 N. Momozawa, J. Phys. Soc. Jpn. 55, 4007 (1986).
20 N. Momozawa and Y. Yamaguchi, J. Phys. Soc. Jpn. 62, 1292 (1993).
21 S. Utsumi, D. Yoshiha, and N. Momozawa, J. Phys. Soc. Jpn. 76, 034704 (2007).
22 E. Tsuji, T. Kuratsawa, I. Yazawa, H. Katoh, N. Momozawa, K. Ishida, and S. Kishimoto, J. Phys. Soc. Jpn. 65, 610 (1996).
23 N. Momozawa, H. Takei, and M. Mita, J. Cryst. Growth 83, 403 (1987).
24 U. Staub, V. Scagnoli, Y. Bodenthin, M. García-Fernández, R. Wetter, A. M. Mulders, H. Grimmer, and M. Horisberger, J. Synchrotron Radiat. 15, 469 (2008).
25 M. Blume and D. Gibbs, Phys. Rev. B 37, 1779 (1988).
26 J. P. Hill and D. F. McMorrow, Acta Crystallogr., Sect. A: Found. Crystallogr. 52, 236 (1996).
27 S. W. Lovesey, E. Balcar, and Y. Tanaka, J. Phys.: Condens. Matter 20, 272201 (2008).
28 Y. Tanaka, T. Takeuchi, S. W. Lovesey, K. S. Knight, A. Chainani, Y. Takata, M. Oura, Y. Senba, H. Ohashi, and S. Shin, Phys. Rev. Lett. 100, 145502 (2008).
29 J. Okamoto, D. J. Huang, C. Y. Mou, K. S. Chao, H. J. Lin, S. Park, S.-W. Cheong, and C. T. Chen, Phys. Rev. Lett. 98, 157202 (2007).
30 Y. Bodenthin, U. Staub, M. García-Fernández, M. Janousch, E. Schierle, V. Soltwisch, D. Schmitz, R. Feyerherm, A. Maljuk, F. Yokaichiya, D. N. Argyriou, and E. Weschke, arXiv:0910.5663 (unpublished).