Origin of the Large Electric Polarization in Multiferroic Orthorhombic $YMnO_3$ Thin Films Revealed by Soft and Hard X-Ray Diffraction

We investigated the magnetic structure of a multiferroic orthorhombic $YMnO_3$ thin film by resonant soft X-ray and hard X-ray diffraction. We observed a temperature-dependent incommensurate magnetic reflection below 45 K and a commensurate lattice-distortion reflection below 35 K. These results demonstrate that the ground state is composed of coexisting *E*-type and cycloidal antiferromagnetic states. Their different ordering temperatures confirm that the origin of the large polarization is the *E*-type antiferromagnetic states in the orthorhombic $YMnO_3$ thin film.

Recently, there has been a lot of interest in multiferroic materials displaying both ferroelectric and magnetic orders [1-3]. It is of particular importance to control magnetization (electric polarization) by an electric (magnetic) field. Orthorhombic (*o*) $RMnO_3$ (*R* denotes rare earth metal) with perovskite structure belongs to this category and can be viewed as a prototypical multiferroic material. The fabrication of *o*-$RMnO_3$ thin films is especially important for the application of multiferroic materials in devices. Recently, Nakamura et al. reported the fabrication of *o*-$YMnO_3$ thin films on a $YAlO_3$ (010) substrate [4]. Their thin film showed a ferroelectric transition at 40 K with a large saturation electric polarization of 0.8 μC/cm^2. The ferroelectric polarization could be controlled by a magnetic field, demonstrating magnetoelectric behavior. In this work, we investigated the magnetic structure of a multiferroic orthorhombic $YMnO_3$ thin film by resonant soft X-ray and hard X-ray diffraction to clarify the exact magnetic structure [5].

A thin film (40 nm) of $YMnO_3$ was grown on a $YAlO_3$ (010) substrate by pulsed-laser deposition. The details of the sample fabrication were described elsewhere [4]. Resonant soft X-ray diffraction experiments were performed on the RESOXS end station at the surface-interface microscopy (SIM) beamline of the Swiss Light Source of the Paul Scherrer Institut, Switzerland. Hard X-ray diffraction experiments were performed on beamlines 3A and 4C at the Photon Factory, KEK, Japan. The photon energy of the incident X-ray was 12 keV.

Figure 1 shows the temperature dependence of the (0 q_b 0) (q_b ~ 0.5) peak with π incident X-ray polarizations. Here, the diffraction data were taken at $h\nu$ = 643.1 eV (Mn $2p_{3/2} \rightarrow 3d$ absorption edge). This peak, which is indicated by vertical bars, appears at 45 K, which coincides with the antiferromagnetic transition temperature T_N determined from magnetization measurements [4]. Weaker peaks are observed on both sides of the reflection. These are antiferromagnetic Kiessig fringes, and describe the limited thickness of the magnetic contrast of the film. The intensity of the peaks increases monotonically with cooling. The peak position deviates from the commensurate q_b = 1/2 position for all temperatures.

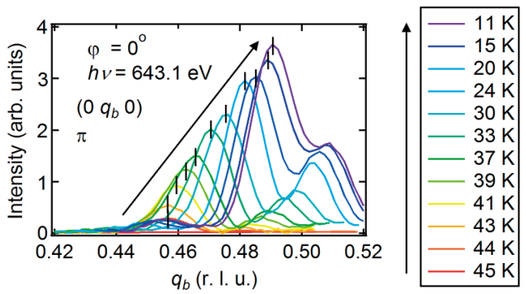

Figure 1
Temperature dependence of the (0 q_b 0) (q_b ~ 0.5) peak in π incident X-ray polarizations. The intensity of the peaks increases monotonically with cooling. The data were taken at $h\nu$ = 643.1 eV (Mn $2p_{3/2} \rightarrow 3d$ absorption edge).

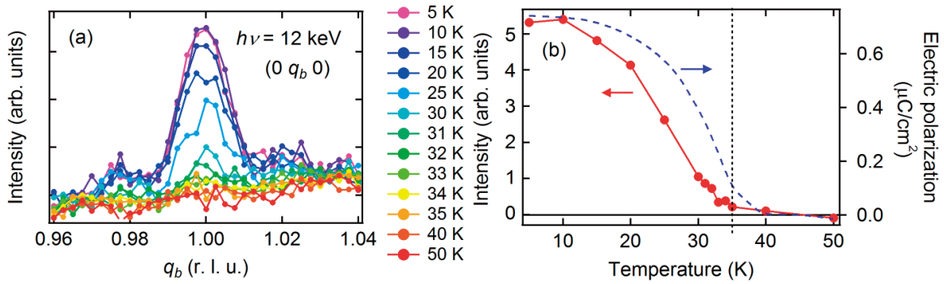

Figure 2
Temperature dependence of the (0 1 0) peak taken at $h\nu$ = 12 keV. In panel (b), peak intensities are plotted as a function of temperature together with the electric polarization (broken lines) taken from Ref. [4]. The temperature of 35 K is also indicated as the onset of the (0 1 0) peak and the step onset of the spontaneous electric polarization.

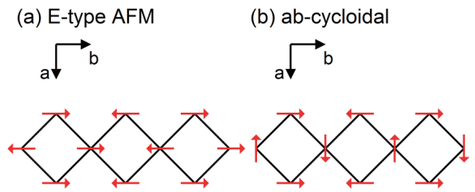

Figure 3
Spin structures in the *E*-type (a) and the *ab*-cycloidal (b) antiferromagnetic states. (a) Spins align antiparallel to each other, resulting in a large lattice strain and large electric polarization. (b) Spins align helically along the *b*-axis, resulting in small electric polarization.

In order to investigate the lattice distortions associated with magnetic order and electric polarization, we performed hard X-ray diffraction measurements of the $YMnO_3$ thin film. The commensurate (0 1 0) reflection appears below 35 K as shown in Fig. 2. This reflection is structurally forbidden in the chemical high-temperature structure (space group: Pbnm) and is caused by the lattice distortion accompanying ferroelectricity. Interestingly, no incommensurability of this reflection is observed by hard X-ray diffraction, in clear contrast to the observed magnetic reflection. Moreover, this reflection does appear below 35 K, at lower temperatures than the onset of the magnetic reflection, in accordance with the step onset of the spontaneous electric polarization [4], as can be seen from the temperature-dependent integrated intensity shown in Fig. 2 (b).

We can obtain a full picture of the magnetic states of the epitaxial $YMnO_3$ thin film by combining the above results with the macroscopic measurements of magnetization and electric polarization [4]. The ground state of the $YMnO_3$ thin film can be explained by the coexistence of the cycloidal and the *E*-type states as shown in Fig. 3 and as theoretically predicted [6]. In this coexistence region, magnetic reflection is incommensurate and lattice peaks are commensurate because the *E*-type phase has a much larger lattice distortion than the cycloidal phase. The existence of the *E*-type phase causes the large electric polarization of 0.8 μC/cm^2 due to the symmetric exchange striction.

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BEAMLINES

3A and 4C

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