Structural investigation of magnetocapacitive SmMnO₃

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Structural deformation of a magnetocapacitive material SmMnO₃ was studied by X-ray diffraction measurement in a magnetic field. This antiferromagnetic material shows a jump in dielectric constant at 9 K only when a magnetic field of a few tesla is applied. In-field X-ray diffraction measurements clarified that there is no sudden change in structure that involves atomic displacement within the *c*-plane in *Pbnm* notation, while the antiferromagnetic phase transition at 60 K gives rise to a noticeable rotation of the MnO₆ octahedra. This rotation occurs to maximize the energy gain through the exchange interaction.

Electric (magnetic) field control of the magnetic (electric) properties allows us to design memory devices that consume very little energy. Such magnetoelectric coupling has been presumed in the 19th century,[1] and a recent report on TbMnO₃[2] has renewed interest in this effect. So far, strong magnetoelectric coupling has been reported in various metal oxides having electric polarization induced by the inverse Dzyaloshinskii-Moriya interaction[3] or the exchange striction.[4] In this context, layered antiferromagnetic (A-type AFM) materials are not expected to have close relationships between magnetism and the dielectric property. However, a large magnetocapacitive effect was recently found in an A-type AFM SmMnO₃.[5] This orthorhombic perovskite (space group: *Pbnm*) shows a paramagnetic to A-type AFM transition at $T_N = 60$ K. The spins are nearly parallel to the *b*-axis, and form a ferromagnetic layer in the *c*-plane with nearly antiparallel arrangement along the *c*-direction.[6] Since the inter-plane spin arrangement is slightly tilted, there is a small spontaneous magnetization in the A-AFM phase. The magnetization is parallel to the external field above 9 K, and it changes its direction to antiparallel (i.e., negative magnetization) below 9 K in a small external magnetic field below 1 T.[5],[7] When a strong magnetic field is applied parallel to the *c*-axis, a flip of the magnetic moment is observed below 9 K. Interestingly, this flip in magnetic moment is accompanied by a sudden change in dielectric constant [**Fig. 1**(a)]. The dielectric property is directly connected to the structure. In fact, a slight change in lattice parameters was observed at the magnetization flipping.[8] This change in lattice parameters may be caused by a large staggered distortion. Thus, we investigated the microscopic structure at the magnetization flipping.

Single crystals of SmMnO₃ were grown by the floating zone method. Single crystal structure analysis data in the absence of magnetic fields were taken at BL-8B at the Photon Factory. Photographs taken with an X-ray whose wavelength was 0.688519(17) Å were processed with RAPID AUTO software, and analyzed with CRYSTAL STRUCTURE (Rigaku). The wavelength was calibrated by using a powder pattern of CeO₂
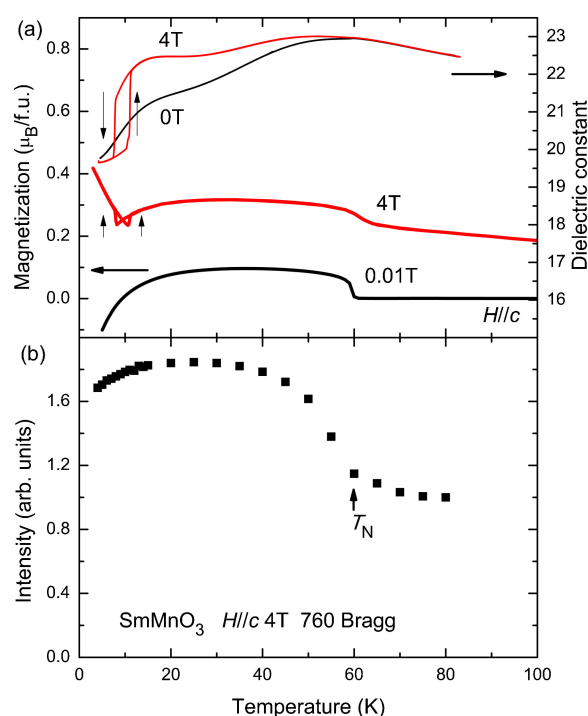

Fig. 1. (Color online) (a) Temperature dependence of the magnetization and dielectric constant of SmMnO₃ measured in high- and weak-magnetic fields. [5] (b) Temperature variation of the 760 Bragg intensity at 4 T.

standard sample. The sample temperature was controlled with a dry N₂ gas flow type sample cooler. X-ray diffraction measurements under a magnetic field were performed at BL22XU at the SPring-8 and BL-3A at the Photon Factory. Both beamlines have a large two-circle diffractometer with an 8 T superconducting magnet that applies the magnetic field perpendicular to the scattering plane. Plate-shaped samples were cut parallel to the *a*- and *b*-planes with diameters of 4 mm.

Table 1 shows the results of the structure analyses at 300 and 100 K in zero magnetic fields. As can be seen, little structural

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Table 1. Results of structure refinement for 300 K 0 T, 100 K 0 T and 20 K 4 T

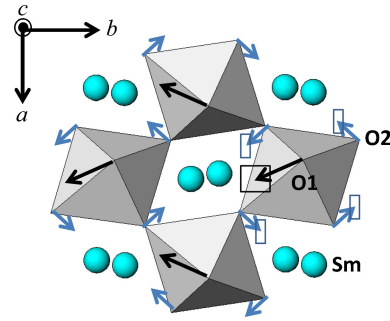| H (T)		4	0	0
T (K)		20	100	300
a (Å)		5.3689(8)	5.365(3)	5.3694(8)
b (Å)		5.8430(9)	5.8541(17)	5.8649(7)
c (Å)			7.468(2)	7.4803(9)
Sm	4c(x,y,1/4)			
x		0.98528(8)	0.98540(4)	0.98515(4)
y		0.0745(2)	0.07567(2)	0.07600(2)
Mn	4b(1/2,0,0)			
O1	4c(x,y,1/4)			
x		0.093(2)	0.0966(6)	0.0977(5)
y		0.480(2)	0.4724(3)	0.4722(3)
O2	8d(x,y,z)			
x		0.2119(8)	0.2085(4)	0.2084(3)
y		0.1796(19)	0.1759(2)	0.1757(2)
z			0.54714(19)	0.54748(17)
Mn–O1–Mn (°)		149.3(8)	147.59(17)	147.25(16)
Mn–O2–Mn (°)		148.6(5)	147.36(8)	147.24(7)
R			0.0333	0.0292

Fig. 2. (Color online) Schematic view of the structural deformation caused by the A-AFM ordering. The arrows show the deformation between 20 K 4 T and 100 K 0 T, and the small boxes show the error.

change was induced by the sample temperature within the paramagnetic phase. Figure 1(b) shows the temperature dependence of the 760 Bragg reflection intensity measured at 4 T. There is a sharp kink at 60 K, the Neel temperature. Since the intensity of Bragg reflections directly reflects the atomic arrangement within a unit cell, this sharp kink in the intensity reflects the structural deformation that arises below the Neel temperature. On the other hand, there is no anomaly at 9 K except for the gradual decrease in intensity. It means that there is no detectable lattice deformation parallel to the (760) direction, while displacements perpendicular to the scattering vector are still allowed.

Because of the narrow window of the superconducting magnet, only the $l = 0$ plane can be accessed. We measured the intensity of various Bragg reflections on the $hk0$ zone as a function of temperature at 4 T of magnetic field. As a result, no sudden lattice deformation at 9 K within the c-plane was found. In other words, the jump in dielectric constant does not involve any change in MnO₆ octahedral rotation or Sm shift within the c-plane. One may want to use the powder diffraction method to access wider reciprocal space. It should be noted that the powder X-ray diffraction method in magnetic fields is useless for the study of microscopic structure, because every single observed peak is coming from crystallites under different orientations of the magnetic field. Specifically, the hkl peak is coming from crystallites in the magnetic field perpendicular to the hkl direction. $00l$ peaks reflect the structural information of crystallites in the magnetic field applied within the a–b plane, $h00$ peaks show the structure under the field in the b–c plane, and so on. X-ray crystallography is based on the intensity data obtained from the sample under a single condition. Therefore, the powder diffraction data taken in a magnetic field is not suitable for detailed analysis.

Let us focus our attention on the structural deformation induced by the A-AFM ordering in the magnetic field. Usually, single crystal structure analysis data are taken with samples smaller than the X-ray beam diameter to minimize optical problems. However, such a small sample is not suitable for in-field study because the sample must be held tightly to prevent the applied field from moving the crystal. In this study, we used plate-shaped crystals with diameters of 4 mm, which is far larger

than the beam size. In order to cancel out any optical problems, Bragg intensity normalized by that measured at 100 K was used for numerical analysis. Since the structure in the paramagnetic phase was found to be constant, we can calculate the peak intensity from this normalized value.

The temperature variation of the intensity was measured at 12 reciprocal points. To reduce the number of unknown parameters, the atomic displacement parameters were assumed to be a small constant value. In the *Pbnm* space group, x and y of Sm (4c site) and O1 (4c site), and x, y, and z of O2 (8d site) are allowed to be modified. The lack of information along the c^*-direction results in the lack of the structural information along the c-direction. Therefore, the parameters we can derive are 6 parameters and the z parameter for O2 site is left unknown.

Our least-squares refinement provides the result shown in Table 1, and the schematic of this result is shown in **Fig. 2**. In this figure, the small arrows show the direction and the magnitude of the atomic displacement induced by the A-AFM order. The length of the arrow is magnified by a factor of 35 for presentation. The boxes at the end of the arrows show the size of the error bar. As can be seen, Sm ions are not moved within the error bar. Mn ions also show no displacement, which is a requirement of *Pbnm* symmetry. All the intensity change was caused by the oxygen displacement. The mode of oxygen displacement makes the Mn–O–Mn angle larger. This mode of deformation makes the energy gain through the exchange interaction larger in A-AFM ordering. Such deformation is expected for all manganites that have A-AFM phases, whereas experimental observation is not very abundant. For example, a structural study[9] on LaMnO₃ does not report clear change in Mn–O–Mn angle at the A-AFM transition, while the temperature variation of the lattice parameter[10] implies that the Mn–O–Mn bond angle tends to be more straight in the A-AFM phase.

In summary, we have performed an X-ray diffraction study in a magnetic field on SmMnO₃ single crystals, and found (1) no distinctive structural change within the c-plane at the spin flipping temperature, and (2) significant rotation of MnO₆ octahedra at the Neel temperature. Our results clearly indicate that the strong coupling between the magnetism and the lattice in this material. This strong coupling is one of the keys to the relationship between magnetism and the dielectric property.

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