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High-field study of multiferroic BiFeO$_3$

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Abstract. We studied the magnetization ($M$) and electric polarization ($P$) in single crystals of BiFeO$_3$ with a unipolar ferroelectric domain in pulsed high magnetic fields up to 55 T. At low temperatures, the application of magnetic fields causes sharp changes in $M$ and $P$ at around 18 T, which can be ascribed to the magnetic transition from a cycloidal to a canted antiferromagnetic state. Measurements of $P$ up to 600 K suggest that this transition disappears as the temperature approaches the Néel temperature. These results indicate that the field-induced change in $P$ originates from the $P$ component generated by the spiral magnetic ordering in BiFeO$_3$. Furthermore, we found that the microscopic magnetoelectric coupling constant of BiFeO$_3$ is greater than those of typical multiferroic materials such as TbMnO$_3$. This fact indicates strong coupling between the magnetic and dielectric properties of BiFeO$_3$.

1. Introduction
The discovery of gigantic magnetoelectric effects has shed new light on ferroelectric magnets [1]. Recent theoretical studies have revealed the presence of spin-driven electric polarization in some types of spatially modulated spin structures [2]. Such modulated spin structures are usually realized in frustrated magnets, and therefore most multiferroic materials become polar only in low-temperature magnetically ordered states. On the other hand, BiFeO$_3$ is known as a unique multiferroic material at room temperature. In this compound, electric polarization ($P$) appears along the [111] direction of the pseudocubic crystal (or along the [001] direction of the hexagonal crystal) below 1100 K [3]. Spins in the Fe$^{3+}$ ions are ordered in a cycloidal structure with a long wavelength (620 Å) at temperatures less than around 600 K [4]. Due to this discrepancy in ordering temperatures, the coupling between $P$ and magnetism is generally considered to be weak. However, Popov et al. have demonstrated sharp changes in $P$ induced by high magnetic fields of approximately 20 T [5]. Since the observed change in $P$ was 3 orders of magnitude smaller than that realized within a single polarization domain at zero field, the quantitative reexamination of $P$ and magnetization is highly desirable. Therefore, in this study, we performed measurements of magnetization and electric polarization in unipolar single crystals of BiFeO$_3$ under high magnetic fields.

2. Experimental
Single crystals of BiFeO$_3$ were grown by the flux method below their ferroelectric Curie temperature in order to obtain a single electric polarization domain. Electrodes were formed by applying silver paste on the as-grown surfaces of platelet crystals [Fig. 1(a)], and therefore, we measured the $P$ component projected on the [001] axis in the pseudocubic notation.
Pulsed magnetic fields of up to 55 T were generated by non-destructive magnets developed at the International MegaGauss Science Laboratory at The Institute for Solid State Physics. Magnetization ($M$) was measured by the induction method using coaxial pick-up coils. Magnetic-field-induced changes in $P$ were detected by measuring the polarization current [6], which was integrated numerically to obtain the values of $P$. Generally, the extrinsic contribution of the voltage induced in electric wiring loops is eliminated with subtracting the data in the paraelectric state. However, in this study, we do not employ this procedure because the Curie temperature of BiFeO$_3$ is higher than the temperature limit of the probe used in this experiment (600 K). In both the experiments of magnetization and electric polarization, magnetic fields ($H$) were applied along one of the principal axes in the pseudocubic crystal [Fig. 1(b)].

3. Results and discussion

Figure 2 shows the field-induced change in $P$ as a function of $H$ applied parallel to the electrode planes. The data shown in Fig. 2 are obtained without the applied voltage. In the sample composing a single ferroelectric domain, we cannot expect to observe a poling effect by applying electric fields. We did not observe any significant change in the $P-H$ curves when an external voltage was applied. In this figure, we only show the data for the field-increasing process to clarify the intrinsic component. At a low temperature, $P$ increases sharply at around 18 T, as reported earlier [5]. The observed change in $P$ ($\sim 50 \, \mu C/m^2$) is several times larger than those reported in Ref. 5, but still less than 1/1000 of the spontaneous values of $P$. $P$ does not exhibit any features of additional transitions with a further increase in $H$ up to 55 T (not shown). Although the sharp change in $P$ appears to be suppressed with an increase in the temperature, the field-induced change in $P$ remains substantial even at 300 K ($270 \, \mu C/m^2$ at 15.6 T). We can identify kinks in the $P-H$ curves up to 550 K, denoted by triangles in Fig. 2.

The isothermal magnetization curves for several temperatures are shown in Fig. 3. The application of magnetic field of 16 — 18 T causes small jumps in $M$. The extrapolation of the $M-H$ curves to $H = 0$ indicates the presence of a finite ferromagnetic component in the high-
field state. These results are consistent with the interpretation of this transition as a change from a cycloidal to a canted antiferromagnetic state [5, 7]. The present results indicate that this interpretation is applicable up to at least 300 K. We performed magnetization measurements up to 55 T at 4.2 K (not shown). The results did not show any additional transitions similar to the results obtained for polycrystalline samples [8]. The temperature dependence of this transition (circles) and that of the kinks in the $P$-$H$ curves (triangles) are shown in Fig. 4. It can be clearly seen that the kinks in the $P$-$H$ curves coincide with the magnetic transition. The transition field decreases as the temperature increases and it seems to disappear as the temperature approaches $T_N$.

Let us discuss the origin of the field-induced change in $P$. As demonstrated above, the change in $P$ is accompanied by the destruction of the cycloidal spin state. In BiFeO$_3$, the origin of this modulated spin order can be attributed to the magnetoelectric coupling rather than the frustration in the exchange interaction. In this system, the density of the Landau-Ginzburg energy can be written as [9]

$$f = -\gamma P_z (l_x \nabla_x l_z - l_y \nabla_y l_z) + A \sum_{x,y,z} (\nabla l_i)^2 - K_u l_z^2 - \frac{1}{2} \chi_\perp H_i^2,$$

where $l$ is the unit antiferromagnetic vector, and $\gamma$, $A$, and $K_u$ are constants representing the magnetoelectric coupling, exchange stiffness, and single-ion anisotropy, respectively. If we neglect the anisotropy and the Zeeman terms, then this equation gives the minimum energy when

$$\phi = \tan^{-1} \left( \frac{q_y}{q_x} \right), \quad \theta = q_x x + q_y y$$

where $q$ is the magnetic wave vector, and $\theta$ and $\phi$ are the polar and azimuthal angles of $l$, respectively. This solution represents the cycloidal state in zero field. The application of $H$ parallel to the direction of $P$ causes a transition to a homogeneous state at

$$H_{[111]c} = \sqrt{\frac{4Aq^2}{\chi_\perp}}.$$
Using \( A = 3 \times 10^{-7} \text{erg/cm}, \ q = 1.0 \times 10^6 \text{cm}^{-1} \) and \( \chi_\perp = 4.7 \times 10^{-5} \) [5], the transition field \( \mu_0 H_{[111]} \) is estimated to be 16 T, which is in reasonable agreement with the experimental results [10].

According to recent theoretical studies [2], spatially modulated spin structures generate \( P \) as

\[
P = \alpha \sum_{(i,j)} e_{ij} \times (S_i \times S_j),
\]

where \( e_{ij} \) is a unit vector connecting the adjacent spins. Combining Eqs. 2 and 4, the cycloidal order in BiFeO\(_3\) generates an additional \( P \) component along the [111] direction of the pseudocubic lattice. In the present study, we observed a field-induced change of \( \sim 270 \mu \text{C/m}^2 \) in \( P \) along the [001] direction (\( \sim 470 \mu \text{C/m}^2 \) along the [111] direction) at room temperature.

By measuring the change in \( P \) in the transition field, we can evaluate the \( P \) component derived from magnetic ordering. We estimate the microscopic magnetoelectric coupling constant \( \alpha = 1.1 \times 10^{-5} \mu \text{C/m}^2 \) for BiFeO\(_3\) at 300 K, where \( \mu \) is the elementary change, by taking into account the actual spin arrangement. This value is 5.5 times that obtained in the case of TbMnO\(_3\) [1].

This result indicates that the magnetoelectric coupling in BiFeO\(_3\) is strong as compared to other multiferroic materials that exhibit gigantic magnetoelectric effects. Studies on other Bi-based materials will provide us with new insights into the magnetic control of ferroelectricity at room temperature.

4. Conclusion
In conclusion, we studied the magnetization and electric polarization of unipolar BiFeO\(_3\) in pulsed high magnetic fields. We observed the change in the electric polarization accompanied with magnetic transition in a wide temperature range. We evaluated the coefficient of magnetoelectric coupling, and found that it was larger as compared to that of those other multiferroic materials.

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[10] The transition field corresponds to \( \mu_0 H_{[001]} = 28 \text{T} \) if we do not take into account the effect of \( \chi_{||} \).