Magnetodielectric effect via a noncollinear-to-collinear spin reorientation in rare-earth iron garnets

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The discovery of ferroelectrics induced by peculiar magnetic structures brought about extensive theoretical and experimental studies. The key driving force for these magnetic ferroelectrics appears to lie in the inverse Dzyaloshinskii-Moriya (DM) interaction in magnets with long-wavelength "noncollinear" spin structures. In this Brief Report, we report the magnetodielectric effect in dysprosium iron garnet which has a noncollinear spin structure within a single unit cell, through the same DM interaction. The distinct effects of magnetism on the lattice are also demonstrated by the unprecedented magnetostriction with a negative Poisson ratio. We attribute the observed magnetodielectric effects and the huge magnetostriction to the magnetic-field-induced spin reorientation from noncollinear to collinear, which possibly weakens the proposed antiferroelectric-type lattice distortion. Our results suggest an additional class of magnetodielectrics and enrich the theoretical understanding of phenomena related to peculiar magnetic structures.

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Owing to the active research on multiferroics in the last few years,[1–3] there has been important progress in the understanding of the mechanism of multiferroics[4–12] and in the observation of various interesting spin-lattice coupling phenomena.[13–17] Derived from these results, recent studies on the application of multiferroics were focused on the design of multiple-state memory or functional devices using the coexistence of magnetism and ferroelectricity.[18–20] On the other hand, in the field of fundamental studies, a lot of effort has been made to understand the microscopic mechanism of multiferroics and the exploration of new multiferroic materials based on the mechanism.[4,10–12]

Among the mechanisms proposed to explain the manifestation of various multiferroics so far, much of the attention has been focused on the mechanism of ferroelectricity induced by magnetism. Here, ferroelectricity is known to be induced by peculiar magnetic structures, which can be classified into two categories.[4] The first is the collinear magnetic structure expected to induce ferroelectricity through the exchange striction mechanism in $R\mathrm{Mn_2O_5}$ (R = rare-earth ion) systems.[6] And the second is the long-wavelength noncollinear magnetic structure known to induce ferroelectricity in various systems like $R\mathrm{MnO_3}$, $\mathrm{CuFeO_2}$, $\mathrm{CoCr_2O_4}$, $\mathrm{Ni_3V_2O_8}$, CuO, etc.[5,7–9,17]

Multiferroics induced by peculiar magnetic structures generally show large magnetoelectric (ME) and/or magnetodielectric (MD) effects due to the change in the magnetic structure when an external magnetic field (H) is applied.[5,16] Thus, these materials have a great potential for novel memories or functional devices in the future. However, the number of candidate materials is very limited for this magnetically induced multiferroic effect because of the very restricted conditions for the peculiar magnetic structures like spin spirals with the wavelength extending over many unit cells. In this sense, materials with noncollinear magnetic structure within a single unit cell could be alternative promising candidates for the MD and ME effects.

Here, we show that the MD and ME effects can be manifested in a ferrimagnetic material, $R_3\mathrm{Fe_5O_{12}}$ (R = rare-earth ion), which has a noncollinear magnetic structure within a single unit cell. Observed anisotropic MD effects in $\mathrm{Dy_3Fe_5O_{12}}$ (DyIG) indicate that the MD effects are related to a noncollinear-to-collinear spin reorientation as well as the magnetic domain rotation. Moreover, we present a clear explanation for the anisotropic MD effect and the huge magnetostriction with a negative Poisson ratio, which results in a significant contraction of the unit cell volume under magnetic fields. We propose antiferroelectricity induced by the noncollinear spin structure within a single unit cell as one of the possible origins of the observed MD and ME effects and the large magnetostriction. Our result may open a new research direction in designing MD-ME materials since the noncollinear spin structure within a single unit cell is more frequently encountered than the one with a long wavelength.

The MD effect in a rare-earth iron garnet system was recently investigated in Tb iron garnets (TbIG), in which a large low-field MD effect was observed.[21] The H dependence of the MD effect in TbIG indicated that the MD effect is closely related to magnetic domain rotation. In addition, the remarkable similarity between the temperature (T) dependence of the MD effect and that of the magnetostriction pointed out that the most probable origin of the large MD effect in TbIG might be the large magnetostriction associated with the rhombohedral distortion below ∼150 K.[22] Although apparently this magnetostriction mechanism explained the qualitative features of the MD effect quite well, it did not elucidate the large quantitative difference between the MD effect and the magnetostriction, and the anisotropic response of the dielectric constants (ε) to the applied H.[21] Therefore there must be another reasonable origin for this complicated MD effect in rare-earth iron garnet systems.

DyIG single crystals used in this experiment were grown by the typical flux method. Thin platelike specimens coated with gold electrodes were used for the measurement of dielectric constant (ε), dielectric loss ($\tan\delta$), polarization, and magnetostriction. ε was measured with a 1–100 kHz ac electric field (E) by using an LCR meter at an excitation voltage of 1 V. The $\tan\delta$ is found to be the order of 10^{-3}. The strain-gauge technique was used to measure the magnetostriction.

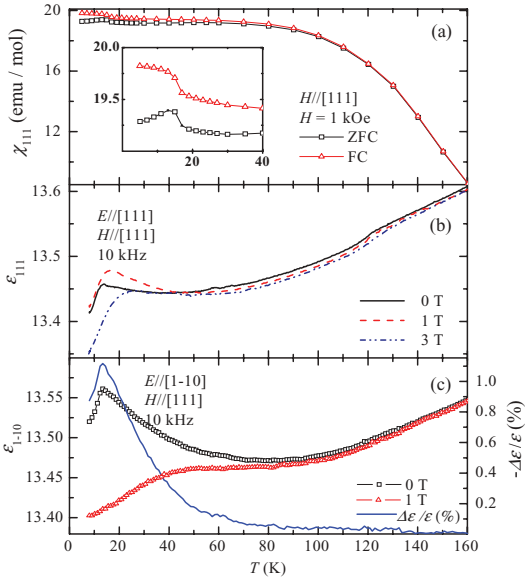

FIG. 1. (Color online) (a) $\chi(T)$ of DyIG along the magnetic easy direction [111] for zero field cooling and $H = 1$ kOe field cooling. Inset: magnified view in the low-T region. (b) $\varepsilon(T)$ measured along [111] in three different H of 0, 1, and 3 T. (c) $\varepsilon(T)$ measured along $[1\bar{1}0]$ in zero H and 1 T applied along the [111] direction, and the corresponding MD effect, $\Delta\varepsilon/\varepsilon = [\varepsilon(1\text{ T}) - \varepsilon(0\text{ T})]/\varepsilon(0\text{ T})$.

In order to investigate the detailed origin of the MD effect in garnet systems, we studied the magnetic and dielectric properties of DyIG. Figure 1(a) shows the T dependence of the magnetic susceptibility (χ) of DyIG along the magnetic easy direction, [111], for zero-field cooling (ZFC) and field cooling (FC) in 1 kOe. As T decreases, χ increases above 80 K, due to the increased exchange interaction between Dy and Fe spins with decreasing temperature.[23] However, below about 80 K, χ exhibits a plateaulike behavior as the Dy spins start to be canted. In addition, at about 17 K it shows a cusplike anomaly which is usually observed at the antiferromagnetic transition. It is believed that the anomaly is related to the long-range noncollinear magnetic ordering of Dy spins with the so-called double-umbrella structure.[24,25] To examine the effect of the magnetic transition on the electric properties, we measured ε of DyIG, shown in Figs. 1(b) and 1(c). ε decreases with decreasing T above 80 K, but starts to increase at low temperatures. Again, it shows a peak at 17 K, where an anomaly appears in χ. The T dependence of the ε data clearly indicates strong coupling between magnetic and electric properties. The MD effects show different behaviors depending on the direction of the ac E used to measure ε. Figure 1(b) shows the T dependence of ε measured along [111], ε_{111}, in magnetic fields along the [111] direction. The H dependence of ε_{111} is rather complicated, i.e., ε_{111} increases in 1 T and decreases again in 3 T. On the other hand, as shown in Fig. 1(c), when E is perpendicular to H, the peaklike feature in $\varepsilon_{1\bar{1}0}$ at 17 K is almost smeared out in H of 1 T and a large negative MD effect reaching ~1% is observed. It is noticeable that the MD effect in Fig. 1(c) starts to increase at ~80 K where χ shows the plateau behavior.

For the interpretation of the complicated T dependence of the MD effect, we measured the H dependence of the magnetic

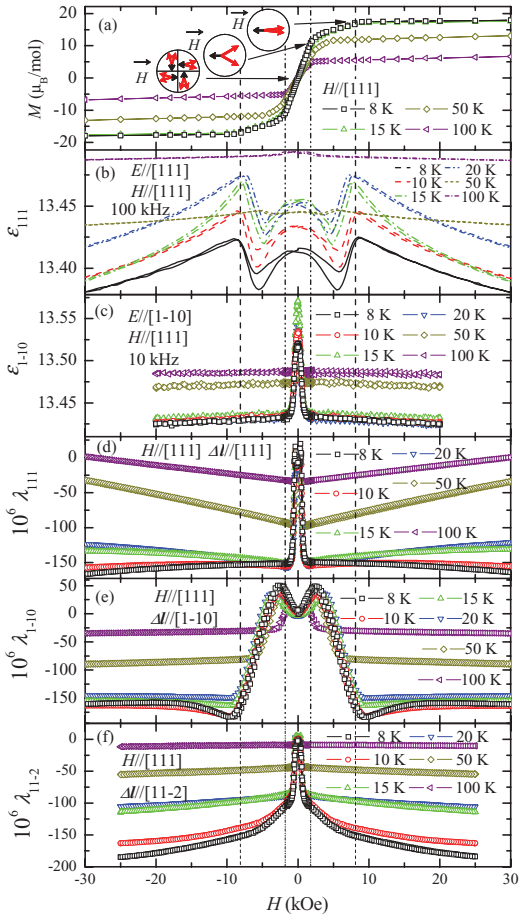

FIG. 2. (Color online) (a) H dependence of M along the magnetic easy direction at four different T's. Insets show the magnetic domains and the spin structure. (b) ε_{111} as a function of H along [111] at various T's. (c) $\varepsilon_{1\bar{1}0}$ as a function of H along [111]. (d) λ_{111} as a function of H along [111]. (e) $\lambda_{1\bar{1}0}$ as a function of H along [111]. (f) $\lambda_{11\bar{2}}$ as a function of H along [111]. The $[11\bar{2}]$ direction is simultaneously perpendicular to [111] and $[1\bar{1}0]$.

and dielectric properties. Figure 2(a) shows the H dependence of magnetization along the magnetic easy axis at various T's. Magnetization exhibiting a linear H dependence in low field showed a kink at around 1.8 kOe and almost saturated at about 8 kOe. It is well known that DyIG has a ferrimagnetic structure, that is, the Dy moments (red arrows in the inset) are aligned antiparallel to the net Fe moment (black arrows in inset).[25,26] Below ~120 K, the canting of Dy moments start to occur with a double-umbrella structure. Considering the canting angles of Dy spins in the double umbrella (13° and 55° at 1.5 K),[24] the observed increase in magnetization between 1.8 and 8 kOe at 8 K (6.16 μ_B/mol) is consistent with the calculated increase of the net magnetic moment (6.23 μ_B/mol) when the spin structure changes from canted to almost collinear. Therefore, we interpret this H dependence of the magnetization as magnetic domain rotation in low field below 1.8 kOe and spin structure change at higher fields between 1.8 and 8 kOe as shown in the insets. We investigated the influence of the magnetic transition on the dielectric properties. Figures 2(b) and 2(c) show the H dependence of ε measured along the [111] and $[1\bar{1}0]$ directions respectively in H applied along

the [111] direction at various T's. ε with E//[111], ε_{111}, does not show any significant change during the domain rotation but it varies greatly during the H-induced change in spin structure between 1.8 and 8 kOe. In higher fields above 8 kOe, ε decreases gradually with increasing H. On the other hand, ε with E//[1$\bar{1}$0], $\varepsilon_{1\bar{1}0}$, decreases abruptly during the magnetic domain rotation in low H and does not change at all in higher H. It is interesting to note that the MD effect has very different H dependence depending on the measurement direction of ε even with the same direction of H. The data in Figs. 2(b) and 2(c) clearly show that there are two different mechanisms of the MD effect in DyIG, i.e., the magnetic domain rotation and the change in the magnetic structure from noncollinear to collinear. Since it should be informative to see the relation between the MD effect and the magnetostriction, we measured the magnetostriction along the [111], [1$\bar{1}$0], and [11$\bar{2}$] directions under applied H along the magnetic easy axis at various T's. The magnetostriction along [111], λ_{111}, showed a significant decrease only in low H during the domain rotation as shown in Fig. 2(d). However, the magnetostriction along [1$\bar{1}$0], $\lambda_{1\bar{1}0}$, exhibited a slight increase in low H and a large decrease in high H during the spin structure change [see Fig. 2(e)]. The magnetostriction along [11$\bar{2}$] , $\lambda_{11\bar{2}}$, exhibited a rapid decrease in low H and a slow decrease in high H during the spin structure change [see Fig. 2(f)]. It is interesting to notice that the H dependence of ε_{111} is very similar to that of $\lambda_{1\bar{1}0}$ while the H dependence of $\varepsilon_{1\bar{1}0}$ is similar to that of λ_{111}. This anisotropic response of ε and λ to the applied H will be discussed below. Note that, despite the similar H dependence of λ and ε, the magnetostriction is smaller than the MD effect by an order of magnitude, which means the MD effect is not wholly due to the simple change of sample dimension caused by the magnetostriction.

The MD effect and the magnetostriction induced by the magnetic domain rotation appear to be natural if we consider the anisotropy in rhombohedrally distorted garnet. However, those induced by the spin structure change seem to have some connection with the magnetically induced ferroelectricity having a long-wavelength noncollinear magnetic structure.[4,10–12] Also, since the peaklike anomalies at 17 K in the ε data in Fig. 1 resemble typical anomalies in the magnetic susceptibility at antiferromagnetic transitions, it is reasonable to assume that the peaklike anomaly in ε might be due to some kind of structural phase transition as well as the indication of antiferroelectricity. In order to check the possibility of antiferroelectricity, we measured the polarization vs electric field (P-E) curve along the [1$\bar{1}$0] direction at low T as shown in Fig. 3(a). The P-E curve showed a linear paraelectric behavior in low E below 180 kV/cm (see the inset). When E is higher than 200 kV/cm, a slight hysteretic behavior starts to appear at one end of the curve, which seems to indicate antiferroelectricity strongly pinned along one direction. This hysteretic behavior was observed in the low-T region below ~80 K where the strong MD effect was detected. When H of 1.2 kOe is applied, the hysteretic behavior becomes much larger and then it completely disappears in higher H of 10 kOe. This H-dependent P-E curve is consistent with the behavior of ε in Fig. 2. In order to discuss the microscopic origin of the interesting MD and ME effects (H-dependent P-E curve), we assume that "magnetically induced antiferroelectricity" is

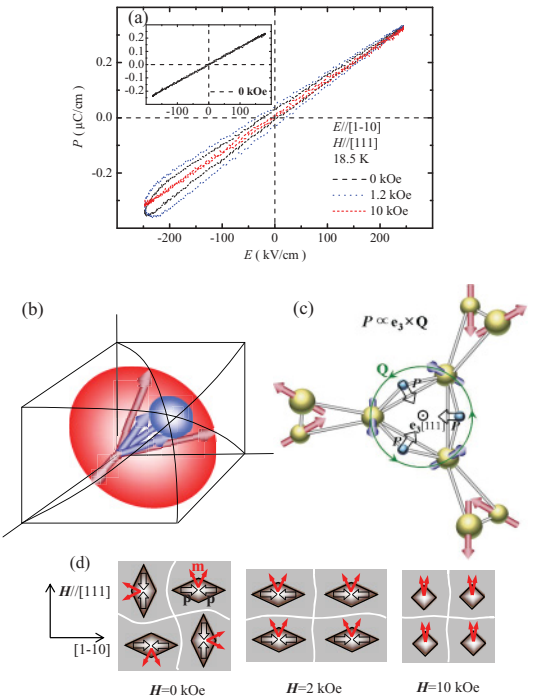

FIG. 3. (Color online) (a) Electric polarization versus electric field (P-E) curve, measured along [1$\bar{1}$0] in three different H's, 0, 1.2, and 10 kOe along [111] at 18.5 K. Inset shows the P-E curve with a lower maximum E. (b) Noncollinear double-umbrella structure of DyIG. (c) Spin structure of Dy ions and the proporsed antiferroelectric distortion viewed along the [111] direction. (d) H dependence of the magnetic and antiferroelectric domains and the lattice distortion.

one of the possible explanations for the observed behavior. Figures 3(b) and 3(c) schematically display the noncollinear double-umbrella structure [Fig. 3(b)] and the basic building block of actual spin arrangement viewed along the [111] direction [Fig. 3(c)].[24] Yellow (blue) spheres indicate Dy (O) ions, and red and blue arrows are Dy spins. Three Dy moments (blue arrows) form a smaller umbrella with a canting angle of 13° and the other three Dy moments (red arrows) form a larger umbrella with canting angle of 55°.[24] Unlike the long-wavelength noncollinear magnetic structure with the wavelength extending over many unit cells, the magnetic structure of Dy spins in garnet is composed of noncollinear spins located at vertices of corner-sharing triangles. In the case of magnetically induced multiferroics, the polarization direction is known to be defined by the cross product of the spin rotation axis ($\mathbf{e}_3$) and the wave vector ($\mathbf{Q}$) through the inverse Dzyaloshinskii-Moriya interaction.[4,10,11] In the present case where noncollinear spins form umbrellas, the spin rotation axis is fixed along the [111] direction. However, since the direction of the modulation wave vector (green arrow) forms a closed loop as shown in Fig. 3(c), the resultant electric dipole or shift of ionic position (black arrows) should change direction at every point on the loop, leaving net zero polarization. This kind of ionic shift may result in antiferroelectriclike lattice distortion. Note that the asymmetric P-E curve at high E in Fig. 3(a) may be due to the triangular arrangement of the electric dipoles. Under applied H large enough to align all spins collinearly, the ionic shift

will be removed and the system will restore its paraelectric state. The reaction of the proposed antiferroelectric distortion to applied H is schematically displayed in Fig. 3(d). Red and black arrows denote Dy moments and electric dipoles in the antiferroelectric arrangement, respectively. The antiferroelectric distortion induced by noncollinear spins forms magnetic and antiferroelectric domains in zero H. When 1.8 kOe H is applied along the magnetic easy axis, those randomly oriented domains will be aligned. This process accompanies a negative (positive) λ along [111] ($[1\bar{1}0]$) due to the domain rotation, as well as a strong negative MD effect along $[1\bar{1}0]$ due to the decreased response of antiferroelectric dipoles parallel to the ac E. When a high H of $\sim$10 kOe is applied, the noncollinear spin structure changes into an almost collinear one, which accompanies the deterioration of the antiferroelectric distortion and negative λ along $[1\bar{1}0]$. It is interesting to notice that the magnetostriction through the magnetic domain rotation in low H is of a normal positive Poisson ratio but the net magnetostriction up to high H is a rare example with an effective negative Poisson ratio,[27] which gives rise to a net decrease in the total volume (λ_{111} and $\lambda_{11\bar{2}}$ exhibit monotonic negative values, and $\lambda_{1\bar{1}0}$ also exhibits a negative value in high H).

The aforementioned scenario may explain all the observed phenomena including the MD (ME) effect and the large magnetostriction in this system. In fact, the giant magnetoelastic coupling recently observed in hexagonal manganites[28] may share a similar origin. Note that the antiferromagnetic ordering in hexagonal manganites has a noncollinear structure in the ab plane, which results in exceptionally large atomic displacements and a strong anomaly in ε measured along the ab plane at the Néel temperature.[28,29]

In summary, we demonstrated that the MD and ME effects can be manifested in DyIG which has a noncollinear magnetic structure within a single unit cell. A mechanism of the MD effect and the magnetostriction in addition to the magnetic domain rotation is suggested, i.e., a noncollinear-to-collinear spin reorientation. We propose that the antiferroelectric-type distortion may underlie the observed MD and ME effects as well as the giant magnetostriction with a negative Poisson ratio. Our result may open a new research direction in designing MD-ME materials and enrich theoretical understanding in the interpretation of phenomena related to peculiar magnetic structures.[30]

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