Experimental observation of magnetoelectricity in spin ice Dy$_2$Ti$_2$O$_7$

L Lin$^{1,2}$, Y L Xie$^1$, J-J Wen$^3$, S Dong$^1$, Z B Yan$^2$ and J-M Liu$^2$

$^1$ Department of Physics & Jiangsu Key Laboratory for Advanced Metallic Materials, Southeast University, Nanjing 211189, People’s Republic of China
$^2$ Laboratory of Solid State Microstructures and Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, People’s Republic of China
$^3$ Institute for Quantum Matter and Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218, USA

E-mail: sdong@seu.edu.cn and liujm@nju.edu.cn

Keywords: multiferroics, spin dynamics, magnetic monopole, spin ice

Abstract

The intrinsic noncollinear spin patterns in rare-earth pyrochlore are physically interesting, due to their many emergent properties (e.g., spin-ice and monopole-type excitation). Recent works have suggested that the magnetic monopole excitation of spin-ice systems is magnetoelectric active, but this fact has rarely been confirmed via experiment. In this work, we performed a systematic experimental investigation on the magnetoelectricity of Dy$_2$Ti$_2$O$_7$ by probing the ferroelectricity, spin dynamics, and dielectric behaviors. Two ferroelectric transitions at $T_{c1} = 25$ K and $T_{c2} = 13$ K were observed. Remarkable magnetoelectric coupling was identified below the lower transition temperature, with significant suppression of the electric polarization on applied magnetic field. Our results show that the lower ferroelectric transition temperature coincides with the Ising-spin paramagnetic transition point, below which the quasi-particle-like monopoles are populated, which indicates implicit correlation between electric dipoles and spin moments. The possible magnetoelectric mechanisms are discussed. Our results can be used for more investigations to explore multiferroicity in these spin-ice systems and other frustrated magnets.

1. Introduction

Spin frustration, which is due to competitive interactions, is common in correlated electronic systems with multifold degrees of freedom [1]. Perhaps the most exciting discovery in spin-frustrated systems in the past decade is the emergence of multiferroicity with strong coupling between ferroelectric and magnetic orders [2–13]. Spin-ice pyrochlores, such as Dy$_2$Ti$_2$O$_7$, are typical highly frustrated magnets, whose structure can be described as a corner-sharing tetrahedron network (see figure 1(a)) [14]. Forced by strong magnetocrystalline anisotropy, each spin points toward or away from the center of the tetrahedron, i.e., Ising-type spin. Although the combination of exchange and dipolar interactions causes the ‘2-in-2-out’ configuration all over the tetrahedron network at low temperatures ($T_S$), the macroscopic degeneracy is unavoidable and results in unusual finite zero-point entropy [15–19]. Furthermore, recent works on thin-film spin ice have shown significant modification of the residual entropy, offering new opportunities for manipulation of the exotic magnetic properties of spin ice [20].

In addition to the zero-point entropy, another interesting magnetic issue in spin ice is magnetic monopole excitation [21–27]. As shown in figure 1(b), an isolated spin-flip generates a ‘3-in-1-out’ and ‘1-in-3-out’ topological defect pair, which breaks the magnetic charge neutrality of the tetrahedron [27]. Such a defect pair, nominally a magnetic monopole-antimonomopole, can separate and move independently without dissipating more energy. The virtual connection between the separated monopole and antimonopole is a Dirac string [24]. Although the experimental evidence of magnetic monopoles can be traced using the neutron-scattering technique [24, 26], the transport of magnetic charges has rarely been investigated, probably due to the difficulty in finding the appropriate macroscopic parameter to characterize the magnetic charges [22, 23, 25].
Polycrystalline Dy$_2$Ti$_2$O$_7$ was prepared using a conventional solid-state method. Stoichiometric mixtures of 2. Details of experimental methods was unknown single crystalline Ho$_2$Ti$_2$O$_7$ although the underlying mechanism remains an open question and needs further study. Structural distortion sustaining at relatively high temperature, and the other one may be the magnetic related, exist. Nonetheless, it can be con microscopic mechanisms are used to interpret the origin of electric polarization, although inconsistencies do identi magnetoelectric coupling. Different from previous reports, two independent ferroelectric transitions are magnetoelectricity for these highly frustrated magnets has yet to be performed.

Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ at low of doped Dy$_2$Ti$_2$O$_7$ samples were prepared under the same conditions, including Dy$_2$... high-purity Dy$_2$O$_3$ and TiO$_2$ were thoroughly ground and heated in air at 1250$^\circ$C for 60 min. The sample at 2 K before the short-circuiting process until the end of the measurements at the rate of 6 K min$^{-1}$. During this process, the background of electrical current was reduced to the minimum level ($\sim 6$ K min$^{-1}$. During this process, the background of electrical current was reduced to the minimum level ($\sim 0.5$ pA).

Very recently, Khomskii proposed a novel mechanism where each monopole (magnetic charge) carried a finite electric dipole in spin-ice systems via the exchange striction mechanism [27]. In addition, another mechanism based on the Dzyaloshinskii-Moriya (DM) interaction has been proposed to generate finite polarization for the noncollinear spin patterns [28, 29]. Our group has reported the polarization of polycrystalline Cr-doped Ho$_2$Ti$_2$O$_7$ at a relatively high $T$ (e.g., up to 140 K), while the microscopic mechanism was unknown [30, 31]. Additionally, one more ferroelectric transition at low $T$ ($\sim 28$ K) has been identified in the single crystalline Ho$_2$Ti$_2$O$_7$ [32]. Saito et al and Katsufuji also found significant magnetodielectric effects in Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ at low $T$s [33, 34]. Despite this isolated evidence, a systematic experimental study of magnetoelectricity for these highly frustrated magnets has yet to be performed.

In this work, we present detailed experiments on ferroelectricity, the dielectric property, spin dynamics, and magnetoelectric coupling. Different from previous reports, two independent ferroelectric transitions are identified at low $T$s (below 25 K), whose magnetoelectric responses are totally different. The available microscopic mechanisms are used to interpret the origin of electric polarization, although inconsistencies do exist. Nonetheless, it can be confirmed that the measured electric polarization has two origins. One is from the structural distortion sustaining at relatively high temperature, and the other one may be the magnetic related, although the underlying mechanism remains an open question and needs further study.

2. Details of experimental methods

Polycrystalline Dy$_2$Ti$_2$O$_7$ was prepared using a conventional solid-state method. Stoichiometric mixtures of high-purity Dy$_2$O$_3$ and TiO$_2$ were thoroughly ground and heated in air at $1250^\circ$C–1400 $^\circ$C with several intermittent heating and grinding steps until a high-quality single phase was obtained. For comparison, a series of doped Dy$_2$Ti$_2$O$_7$ samples were prepared under the same conditions, including Dy$_2$x−Gd$_x$Ti$_2$O$_7$, Dy$_2$−x−TB$_x$Ti$_2$O$_7$, and Y$_2$Ti$_2$O$_7$.

For electric measurements, each sample was first polished into a disk 0.2 mm thick and then coated with Au on each side as electrode. The crystal structure was checked by x-ray diffraction (XRD) (Bruker Corporation) with Cu $K\alpha$ radiation. All the reflections were assigned to the single-phase cubic pyrochlore structure. The dielectric measurements were performed using the HP4294A impedance analyzer associated with Physical Properties Measurement System (PPMS) (Quantum Design, Inc). The ac magnetic susceptibility (real part $\chi'$ and imaginary part $\chi''$) was measured on a powder sample using the PPMS system with the ACM option (frequency $f = 10$ Hz $\sim 10$ kHz).

The electric polarization ($P$) was measured using a high-precision pyroelectric current method. The sample was first poled under an electric field ($E_{pol} = 10$ kV cm$^{-1}$) and cooled down from 100 K to 2 K. Then the electric field was removed, followed by sufficiently long short-circuiting (60 min at 2 K, i.e., a relaxation of the spin structure for 60 min). During this process, the background of electrical current was reduced to the minimum level (i.e., $<0.5$ pA). The $P$ was obtained by integrating the pyroelectric current ($I$) through warming the sample at 2 K min$^{-1} \sim 6$ K min$^{-1}$, using a Keithley 6514 electrometer connected to PPMS [35]. This data was taken from the measurements at a rate of 2 K min$^{-1}$, implying a time scale of 14 min from 2 K to 30 K. For the pyroelectric current measurement under a constant magnetic field ($H$), the assigned field $H$ was applied to the sample at $T = 2$ K before the short-circuiting process until the end of the measurements at the rate of 2 K min$^{-1}$. We also measured the isothermal polarization $P$ against $H$. The sample was first electrically poled and cooled down to an assigned $T$ with $H = 0$, and then the electric field was removed, followed by sufficiently long
short-circuiting (60 min at 2 K, i.e., a relaxation of the spin structure for 60 min). The released magnetoelectric current upon increasing $H$ from $H = 0$ to $H = \pm 9$ T at a rate of 100 Oe/s was collected.

3. Results

3.1. Dielectric and ferroelectric properties

We first address the dielectric and ferroelectric data on Dy$_2$Ti$_2$O$_7$. The dielectric constant ($\varepsilon$) at low $T$ is presented in figure 2(a), and its insert shows the dielectric data in a broader $T$ region. The $\varepsilon(T)$ increases gradually with decreasing $T$, and interestingly, two broad anomalies are identified roughly at $T_{c1} \sim 25$ K and $T_{c2} \sim 13$ K, respectively, which implies possible ferroelectric transitions at these points.

To confirm these ferroelectric transitions, the pyroelectric current $I(T)$ data at three different warming rates (2, 4, and 6 K min$^{-1}$) are plotted in figure 2(b). Each curve shows two clear peaks right below $T_{c1}$ and $T_{c2}$, without significant peak shift (only 0.7 K shift for the high-$T$ peak between 2 K min$^{-1}$ and 6 K min$^{-1}$) along the $T$-axis for different warming rates. It is noted that a tiny shift (e.g., < 1.0 K) of the $I$-$T$ curve to the high-$T$ side is inevitable. For example, during the warming process, especially for the high rate (e.g., 6 K min$^{-1}$), we can’t exclude the tiny temperature difference between the sample and the thermocouple attached aside the sample. The temperature difference between the inside sample and thermocouple becomes larger when the warming rate is higher. Since the recorded temperature step is $\sim$0.1 K and the practical reasons described above, the extrinsic contribution, if any, should be very weak, and will not affect our physical conclusion. The polarizations integrated from these pyrocurrents are almost identical for different warming rates, which implies that the measured $I(T)$ comes from the pyroelectric effect associated with the electric polarization [36]. The complete reversal of $P$ is demonstrated by using the negative poling fields ($E_{pole} = \pm 10$ kV cm$^{-1}$), as shown in figure 2(c).

The first ferroelectric transition occurs at $T_{c1}$ with a saturated pyroelectric $P \sim 1.5 \mu$C m$^{-2}$ and the second transition appears at $T_{c2}$ with a saturated $P \sim 3.65 \mu$C m$^{-2}$ at 2 K.
Since the Dy$_2$Ti$_2$O$_7$ exhibits two ferroelectric transitions at $T_c^1$ and $T_c^2$, the characteristics of these transitions are studied by a series of specially designed experiments, including measuring the magnetoelectric response, modulating the spin-ice configurations through Dy’s site substitutions, and characterizing the magnetic relaxation by ac magnetic susceptibility.

### 3.2. Magnetoelastic response

The response of pyroelectric current $I$ to magnetic field $H$ helps prove magnetoelectricity. Figure 3(a) shows the measured $I(T)$ data under $H = 0, 2, 5, 7, 9$ T, respectively. A prominent feature is that the peak just below $T_c^2$ gradually shifts toward the low-$T$ side and the peak height is suppressed with increasing $H$, while the peak just below $T_c^1$ remains stationary even at $H = 9$ T. This suggests that the ferroelectric transition at $T_c^2$ is magnetically relevant, while at $T_c^1$ it may not be. A possible origin for the ferroelectric transition at $T_c^1$ is purely structural relevant rather than spin relevant.

The evaluated $P(T)$ curves under different $H$ are plotted in figure 3(b) for magnoelectric response. The $P$ is significantly suppressed by $H$ below $T_c^2$, but this suppression is much weaker above it. The decrease of $P$ under $H = 9$ T is maximal ($\approx 25\%$) at $T = 2$ K. In addition, we investigate the magnetoelectric response in the isothermal mode. In figures 4(a)–(b), the measured $P$ and $P(H)$ at $T = 2$ K is plotted, while the whole $P$ response to $H$ in one $H$ cycle between $-9$ T and $9$ T is plotted in figure 4(c). It is clear that during the whole cycle, $P$ is gradually suppressed when increasing $H$, and shows remarkable path-dependent behavior. The irreversible variation of $P$ upon the $H$-cycling may be due to a sequence associated with the magnetic domain wall motion driven by varying $H$.

This irreversibility of magnetoelectric response is rather weak above $T_c^2$, proven by two sets of $I(T)$ data (before and after the $H$-cycling at 2 K) for the same sample, as shown in figure 4(d). It is clear that the peak just below $T_c^1$ remains identical for these two cases, and just below $T_c^2$ it is partially suppressed by the $H$-cycling. We can then conclude that the ferroelectric transition at $T_c^1$ is relevant but that at $T_c^2$ it is not.

### 3.3. Roles of Dy$^{3+}$ ions

The role of Dy$^{3+}$ ions is key to understand the magnetoelectricity. In this section, we modulate Dy$_2$Ti$_2$O$_7$ properties by substituting the Dy$^{3+}$ ion with other magnetic or nonmagnetic rare-earth species. First, we use the nonmagnetic Y$_2$Ti$_2$O$_7$ for comparison, noting that Y$^{3+}$ ion (0.900 Å in ionic radius) is only slightly smaller than Dy$^{3+}$ ion (0.912 Å in ionic radius). The measured $I(T)$ data for Y$_2$Ti$_2$O$_7$ using the same protocol is plotted in figure 5(a) and compared with the data of Dy$_2$Ti$_2$O$_7$. Clearly, there is no pyroelectric current detected for Y$_2$Ti$_2$O$_7$ over the whole measured $T$-range, which suggests that Dy$^{3+}$ ion is the core ingredient for the polarization generations at $T_c^1$ and $T_c^2$.
Second, we turn to the Tb-substituted Dy$_2$Ti$_2$O$_7$, Dy$_{2-x}$Tb$_x$Ti$_2$O$_7$. Using the $x = 0.5$ sample as an example, the pyroelectric data is also shown in Figure 5(a) for comparison. We know the magnetic ground state of Tb$_2$Ti$_2$O$_7$ remains a cooperative paramagnet or spin-liquid state until extremely low $T$ (e.g., 0.07 K), with neither long-range Néel order nor spin-glass ordering [38], which is significantly different than Dy$_2$Ti$_2$O$_7$'s spin-ice magnetic structure. In our Dy$_{2-x}$Tb$_x$Ti$_2$O$_7$ sample, the Tb$^{3+}$ substitution remarkably suppresses the two current peaks, which disappear completely when $x > 1.0$ (not shown).

Third, similar phenomena are also observed for the Gd-substituted Dy$_2$Ti$_2$O$_7$, Dy$_{2-x}$Gd$_x$Ti$_2$O$_7$. Since Gd$_2$Ti$_2$O$_7$ is a typical Heisenberg spin system, Gd$^{3+}$ ($S = 7/2$) has half-filled 4f shell and zero orbital
momentum, i.e., the Gd$^{3+}$ spins can rotate freely in three-dimensional space. Figure 5(b) shows the measured $I(T)$ data for several Dy$_{2-x}$Gd$_x$Ti$_2$O$_7$ samples [39]. The two peaks are significantly suppressed and nearly disappear when $x > 1.4$.

The gradual disappearance of the transition at $T_{c2}$ and $T_{c1}$ is less than expected since we expect the spin-ice structure to be corroded by the Tb$^{3+}$ or Gd$^{3+}$ substitution. As noted before, the transition at $T_{c1}$ may be due to the lattice distortion rather than the magnetic structure. Since the Re$_2$Ti$_2$O$_7$ (Re: rare earth ion) family belongs to the same space group Fd-3m, and the Re$^{3+}$ and Ti$^{4+}$ ions occupy the 16d and 16c positions, respectively, the Raman active modes only involve the O ion vibrations. In fact, Raman spectroscopy on Dy$_2$Ti$_2$O$_7$ in the low $T$ range reveals a new mode, characterizing a phonon softening below $\sim 110$ K and accompanied with a structural transformation [40, 41]. No such phonon mode softening is identified in Gd$_2$Ti$_2$O$_7$ and Tb$_2$Ti$_2$O$_7$ [40]. Thus, the previous Raman studies helped to understand the transition at $T_{c1}$, although no firm conclusions can be made.

3.4. AC magnetic susceptibility

Now we turn to the spin-relevant ferroelectric transition at $T_{c2}$. The above data and discussions have demonstrated the correlation of this transition with the particular spin structure of Dy$_2$Ti$_2$O$_7$ in the low-$T$ range. However, the microscopic details of this correlation remain an open issue. Recently, transverse field muon spin rotation ($\mu$SR) [32] and ac susceptibility methods [23, 42–47] have been used to probe the dynamics of magnetic monopoles in spin ice. Here, to further enhance our understanding of the emergence of multiferroicity in Dy$_2$Ti$_2$O$_7$, a series of measurements on the ac magnetic susceptibility of Dy$_2$Ti$_2$O$_7$ and Gd-substituted Dy$_2$Ti$_2$O$_7$ systems are carefully performed.

The measured characteristic relaxation time ($\tau$) of Dy$_2$Ti$_2$O$_7$ was evaluated by the reciprocal of the maximum $\tau = 1/f_{\text{max}}$ in the dielectric imaginary part $\chi''(f)$ curve, where $f_{\text{max}}$ is the peak frequency. The $\tau$-$T$ dependence curve is presented in figure 6. A clear plateau region between 4 K and 13 K is seen, in which massive magnetic monopoles excite via quantum tunneling [23]. Generally, there are two contributions to magnetic monopole: the ‘single-charged’ monopoles (connected through Dirac string) and the ‘double-charged’ (magnetic monopole pair). At high $T$, the proliferation of bound defects will both disrupt existing strings and reduce the mean-free path for diffusing monopoles [26]. Theoretical works [23, 42] also provide strong evidence that the ‘quantum tunneling’ regime in the magnetic relaxation measurement can be interpreted entirely in terms of the diffusion motion of monopoles, constrained by a network of ‘Dirac strings’.

After further decreasing $T$ below 4 K, a gradual spin freezing of 2- in-2-out configuration starts to emerge and fully evolve into a spin-ice state below 1.1 K (note that there are massive monopole excitations in the temperature region 2 K < $T$ < 4 K). Such a sharp increase of $\tau$ suggests that the thermal relaxation process becomes important due to the strongly correlated spin-spin interactions [44, 47]. For the high $T$ regime ($>13$ K), a sharp drop of $\tau$ with increasing $T$ occurs, indicating another thermal relaxation process [23].

For comparison, a series of Dy$_{2-x}$Gd$_x$Ti$_2$O$_7$ samples with $x \in [0, 2]$ are studied to reveal the spin dynamics in Gd-doped Dy$_2$Ti$_2$O$_7$. The previously discussed ferroelectric property shows that a slight Gd doping level $x$ can significantly suppress ferroelectric phase. Using the $x = 1.1$ sample as an example, the real part $\chi' (T)$ (figures 7(a’)–(d’)) and imaginary parts $\chi''(T)$ (figures 7(a”)–(d’)) under several magnetic fields are plotted. No spin freezing behavior is observed within the selected frequencies at zero magnetic field. However, the imaginary part of susceptibility shows a sharp increase at low temperature, which indicates a strongly dissipative process.

![Figure 6. The characteristic relaxation time $\tau$, as a function of $T$ in absence of magnetic field.](Image)
occurs below 2 K [48]. When the magnetic field increases to 1 Tesla, two clear dips at 3 K, 13 K emerge, identified as $T_f$, $T^*$, and $T_s$ denote the low-temperature spin freezing into ice state, the freezing peak associated with Gd$^{3+}$, and the single-ion peak associated with Dy$^{3+}$, respectively.

Figure 7. The upper (a′)–(d′) and lower (a″)–(d″) panels present the real and imaginary part of $\chi$ susceptibility of Dy$_{0.8}$Gd$_{1.2}$Ti$_2$O$_7$ at selected magnetic fields. $T_f$, $T^*$, and $T_s$ denote the low-temperature spin freezing into ice state, the freezing peak associated with Gd$^{3+}$, and the single-ion peak associated with Dy$^{3+}$, respectively.

Figure 8. Contour plot of imaginary part of $\chi$ susceptibility of Dy$_{2-x}$Gd$_x$Ti$_2$O$_7$ samples at $H = 2$ T measured at $f = 10$ kHz. The $x$–$T^*$ and $x$–$T_s$ relations are shown.

occurs below 2 K [48]. When the magnetic field increases to 1 Tesla, two clear dips at 3 K, 13 K emerge, identified as $T_f$, $T^*$, respectively. At $H = 2$ T, another high-temperature peak (indicated by the $T_s$) shows up at $\sim 25$ K. Here, the two peaks $T_f$ and $T_s$ should have the same origin as those in pure Dy$_2$Ti$_2$O$_7$, and the newly developed $T^*$ should be originated from Gd$^{3+}$, which alters the local Dy-Dy interactions and corresponding crystal field effects. Similar features are also observed in other substituted samples.

The contour plot of $\chi''(T)$ at $H = 2$ T is shown in figure 8 as a function of substitution and temperature. It can be clearly seen that $T^*$ exists in a large region with increasing $x$, while $T_f$ gradually disappears when $x > 1.1$ (the pyroelectric current nearly disappears when $x > 1.4$). The nearly one-to-one correspondence between the appearance of polarization and $T_s$ indicates hidden correlations between spin dynamics and ferroelectricity in spin-ice.

4. Discussion

Although no well-defined clue of the transition at $T_{c1}$ is obtained at this stage, the above experimental data demonstrates the correlation of the ferroelectric transition at $T_{c2}$ with the particular spin structure of Dy$_2$Ti$_2$O$_7$. Thus, we discuss the possible origins of ferroelectric polarization below $T_{c2}$, while the origin for that at $T_{c1}$ is left for future investigation.
4.1. Magnetic monopole

The magnetic monopoles and their cooperative behavior may be one of the origins of the observed magnetoelectric effects. According to Khomskii’s theory, each monopole (magnetic charge) carries a finite electric dipole in spin-ice systems \[27\]. The electric charge transfer (i.e., electric dipole) on any site \(i\) can be written as:

\[
\delta q_i \propto 2 S_i \cdot \left( S_i^+ + S_i^- + S_i^0 \right) - 2 \left( S_i^+ \cdot S_i^- + S_i^0 \cdot S_i^0 \right) \tag{1}
\]

where \(S_i (i = 1-4)\) is the spin. We consider four possible spin configurations as shown in figure 9(a). No charge transfer is available (\(\delta q_i = 0\)) for the configurations (1) (4-in or 4-out) and (4) (2-in/2-out), while finite electric charge transfers (\(\delta q_i \neq 0\)) can be generated in the configurations (2) (3-in/1-out) and (3) (1-in/3-out).

Due to the electric and magnetic nature of monopole, it can be flexibly moved by external electric/magnetic fields. For example, take the lattice shown in figure 9(b), where three electric dipoles are available under zero electric field. When applying a poling electric field \(E\) to the lattice, these dipoles will be polarized to lower the electrostatic energy. These processes can be achieved via one-step motions of the two monopoles. As shown in figure 9(c), two spin-flip events annihilate original dipoles 2 and 3 and create dipoles 4 and 5. When these electric dipoles in the lattice are polarized, a finite macroscopic electric polarization is obtained.

According to previous neutron studies, the spins of \(\text{Dy}^{3+}\) become the Ising-type due to the strong magnetocrystalline anisotropy below 13 K \[26, 49\], consistent with \(T_{c2}\). Therefore, the magnetism-related ferroelectric polarization emerges in the temperature region with massive excitation of monopoles. Of course, there may be some correlation between monopoles and ferroelectricity, a hypothesis that is consistent with the tentative examination of \(\text{Gd}/\text{Tb}\) substituted \(\text{Dy}_2\text{Ti}_2\text{O}_7\) shown in figure 5. Thus, reasonable modulation of ferroelectricity is expected within this scenario.

Although the poling process before pyroelectric current measurement can polarize these monopole-carried dipoles, it is unclear why their orientations can persist after the removal of electric field. The simple dipole-dipole interactions usually depolarize the macroscopic polarization. As shown by figure 8, the magnetic

![Figure 9](image-url)

Figure 9. (a) The specific spin configurations of tetrahedra: (1) 4-in or 4-out, (2) 3-in-1-out, identified as magnetic monopole, (3) 1-in-3-out, as antimonopole, and (4) 2-in-2-out (the spin-ice state). Only cases (2) and (3) carry an electric dipole, indicated by the green arrows. The schematic diagram of the monopole distribution under (b) zero electric field \((E = 0)\) and (c) finite electric field \((E \neq 0)\). (f) The schematic of spin-ice state of \(\text{Dy}_2\text{Ti}_2\text{O}_7\), projected down the a axis. The ‘+’ and ‘−’ signs indicate whether the component of each spin is parallel or antiparallel to the a axis. The yellow arrow presents the generated polarization between the neighbor spins \(S_i\) and \(S_j\) by inverse DM interaction.
The dynamics of Dy$_2$Ti$_2$O$_7$ are quite fast above 5 K. In the absence of electric or magnetic field, the magnetic relaxation should be very fast in the $T$ region, which should lead to the rapid dissipation of polarization with time. Thus, we conducted additional experiments to check the possible evolution of polarization with time. Figure 10(a) shows the time dependence of pyroelectric current at 2 K. This process can be sustained for at least one hour, which is long enough to let the spin fully relax. Subsequently, during the pyroelectric measurement with increasing temperature from 2 K at the rate of 2 K min$^{-1}$, we stopped the warming of the sample and annealed it at 5 K several times (from 1 min until 30 min) and then continued the temperature increase. We did not observe any difference of the $P$-$T$ curves, as shown in figure 10(b) for three cycles of measurements. In this sense, the polarized state is stable, without time-dependent relaxation in such a time scale. If our observed ferroelectricity is due to the Khomskii’s monopole mechanism, there should be some unrevealed couplings that maintain the polarized state.

Our experiment also found that the magnetization is nearly saturated under high magnetic field (e.g., 9 T). In this case, all spins are nearly aligned in one direction, breaking the ice rule and monopole conditions. If the ferroelectricity is caused by monopoles, the Ising-like spin pattern should be significantly damaged by such a strong magnetic field. However, our measurement only found moderate modulation $\sim 25\%$ (figure 3), which cannot be understood from the monopole aspect.

4.2. Spin–orbit couplings: DM interaction & $p$-$f$hybridization

From another point of view, we can see that the spin chain along each of the $\langle 111 \rangle$ axes is noncollinear below $T_{c2}$ and the inverse DM interaction is active due to the Dy$^{3+}$-$\text{O}^{2-}$-$\text{Dy}^{3+}$ pair with bonding angle $109.47^\circ$ [30]. Thus, an electric dipole can be generated for each Dy$^{3+}$-$\text{O}^{2-}$-$\text{Dy}^{3+}$ pair due to the noncollinear spin pair [28, 29], as shown schematically in figure 9(d). The overall polarization is the summation of all these dipoles, which depends on the particular spin patterns. For example, in figure 9(d), the total polarization can be cancelled out or polarized. In this sense, the ferroelectricity relies on the noncollinear spin texture, but not on the monopole excitation.

The magnetic field can align the spins and thus suppress the polarization, which qualitatively agrees with our observation under magnetic field. However, quantitative analysis of this magnetoelectric response is unavailable. Similar to the above monopole theory, it is also unclear why the macroscopic polarization can be stabilized after the electric poling. The dynamics of spins can quickly relax the alignment of dipoles, in contrast to our observations.

The third possible scenario is the single-site $p$-$d$ hybridization-induced polarization proposed by Arima [50]. If this mechanism can be extended to the $p$-$f$ electrons systems, it may generate a polarization. However, since the four nearest-neighbor $\text{O}^{2-}$-$\text{Dy}^{3+}$-$\text{O}^{2-}$ angles are all $180^\circ$, the $p$-$f$ hybridization mechanism cannot be attributed to net polarization due to the intercancellation of these dipoles.

In summary, although we have applied several established theories and scenarios to understand our experimental results, none of them are fully consistent. In the current stage, very little knowledge of the...
ferroelectricity for these systems is available, which means further experimental and theoretical works are in order.

5. Conclusion

In summary, we performed systematic experimental investigation on the ferroelectricity and magnetoelectric coupling effect in spin–ice Dy$_2$Ti$_2$O$_7$. Two ferroelectric transitions were observed. One is from the structural distortion sustained at relatively high temperature, and the other one may be the magnetic related. The origin of ferroelectricity was discussed based on the magnetic monopole scenario and other possible mechanisms. However, the real physical mechanism remains an open question and requires more research. Our results will thus stimulate more investigation on magnetoelectricity in spin-ice systems and other highly frustrated magnets.

Acknowledgments

The authors would like to thank Prof Collin Broholm, Dr Seyed Koohpayeh, and Referee 2 for helpful discussions. Research was supported by the National Natural Science Foundation of China (Grant Nos. 11374147, 51332006, 11234005, 11504048, 51322206), the Jiangsu Key Laboratory for Advanced Metallic Materials (Grant No. BM2007204), post-doctoral Science Fund of China (Grant No. 2015M571630), and post-doctoral Science Fund of Jiangsu Province (Grant No. 1402043B). Work at IQM was supported by the US Department of Energy, office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Grant No. DE-FG02-08ER46544.

References

[1] Gardner J S, Gingras M J P and Greedan J E 2010 Rev. Mod. Phys. 82 53
[2] Cheong S W and Mostovoy M 2007 Nat. Mater. 6 13
[3] Kimura T 2007 Annu. Rev. Mater. Res. 37 387
[4] Wang K F, Liu J M and Ren Z F 2009 Adv. Phys. 58 321
[5] Dong S and Liu J M 2012 Mod. Phys. Lett. B 26 1320004
[6] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 Nature 426 55
[7] Hur N, Park S, Sharma P A, Ahn J S, Guha S and Cheong S W 2004 Nature 429 392
[8] Lee M, Choi E S, Huang X, Ma J, Cruz C R D, Matsuda M, Tian W, Dun Z L, Dong S and Zhou H D 2014 Phys. Rev. B 90 224402
[9] Ye F, Fishman B S, Fernandez-Baca J A, Podlesnyak A A, Ehlers G, Mook H A, Wang Y Q, Lorenz B and Chu C W 2011 Phys. Rev. B 83 140401
[10] Katsura H, Nagaosa N and Balatsky A V 2005 Phys. Rev. Lett. 95 057205
[11] Sergienko I A and Dagotto E 2006 Phys. Rev. B 73 094434
[12] Choi Y J, Yi H T, Lee S, Huang Q, Kiyukhin V and Cheong S W 2008 Phys. Rev. Lett. 100 047601
[13] Lee N, Vecchini C, Choi Y J, Chapon L C, Bombardi A, Radaelli P G and Cheong S W 2013 Phys. Rev. Lett. 110 137203
[14] Harris M J, Bramwell S T, McMorrow D F, Zeiske T and Godfrey K W 1997 Phys. Rev. Lett. 79 2554
[15] Hertog B C D and Gingras M J P 2000 Phys. Rev. Lett. 84 3430
[16] Bramwell S T and Gingras M J P 2001 Science 294 1499
[17] Ramirez A P, Hayashi A, Cava R J, Siddharthan R and Shastry B S 1999 Nature 399 333
[18] Zhou H D et al 2011 Nat. Commun. 2 478
[19] Ke X, Freitas R S, Ueland B G, Lau G C, Dahiøberg M L, Cava R J, Moessner R and Schiffer P 2007 Phys. Rev. Lett. 99 137203
[20] Bovo L, Moya X, Prabhakaran D, Soh Y A, Boothroyd A T, Mathur N D, Aeppli G and Bramwell S T 2014 Nat. Commun. 5 3439
[21] Castelvovo C, Moessner R and Sondhi S L 2008 Nature 451 42
[22] Bramwell S T, Giblin S R, Calder S, Aldus R, Prabhakaran D and Fennell T 2009 Nature 461 956
[23] Jauhert I D C and Holdsworth P C W 2009 Nat. Phys. 5 258
[24] Morris D J et al 2009 Science 326 411
[25] Giblin S R, Bramwell S T, Holdsworth P C W, Prabhakaran D and Terry I 2011 Nat. Phys. 7 252
[26] Fennell T, Deen P W, Wildes A R, Schmalzl K, Prabhakaran D, Boothroyd A T, Aldus R J, McMorrow D F and Bramwell S T 2009 Science 326 415
[27] Khomskii D I 2012 Nat. Commun. 3 904
[28] Dzyaloshinskii I 1958 J. Phys. Chem. Solids 4 241
[29] Moriya T 1960 Phys. Rev. 120 91
[30] Dong X W, Dong S, Wang K F, Wan J G and Liu J M 2010 Appl. Phys. Lett. 96 242904
[31] Dong X W, Wang K F, Luo S J, Wan J G and Liu J M 2009 J. Appl. Phys. 106 104101
[32] Liu D, Lin L, Liu M F, Yan Z B, Dong S and Liu J M 2013 J. Appl. Phys. 113 171901
[33] Saito M, Higashinaka R and Maeno Y 2005 Phys. Rev. B 72 144422
[34] Katsufuji T and Takagi H 2004 Phys. Rev. B 69 064422
[35] Lin L, Zhu H X, Jiang X M, Wang K F, Dong S, Yan Z B, Yang Z R, Wan J G and Liu J M 2014 Sci. Rep. 4 6530
[36] Zhang G Q, Dong S, Yan Z B, Guo Y Y, Zhang Q F, Yunoki S, Dagotto E and Liu J M 2011 Phys. Rev. B 84 174413
[37] Park S, Choi Y J, Zhang C L and Cheong S W 2007 Phys. Rev. Lett. 98 057601
[38] Gardner J S, Gaulin B D, Berlinsky A J, Waldron F, Dunsiger S R, Raju N P and Greedan J E 2001 Phys. Rev. B 64 224416
[39] Lin L, Zhao Z Y, Liu D, Xie Y L, Dong S, Yan Z B and Liu J M 2013 J. Appl. Phys. 113 113903
[40] Kamaraju N, Kumar S, Saha S, Singh S, Suryanarayanan R, Revcolevschi A and Sood A K 2011 Phys. Rev. B 83 134404
[41] Saha S, Singh S, Dkhil B, Dhar S, Suryanarayanan R, Dhalenne G, Revcolevschi A and Sood A K 2008 Phys. Rev. B 78 214102
[42] Jaubert L D C and Holdsworth P C W 2011 J. Phys.: Condens. Matter 23 164222
[43] Bovo L, Bloxsom J A, Prabhakaran D, Aeppli G and Bramwell S T 2013 Nat. Commun. 4 1535
[44] Snyder J, Ueland B G, Slusky J S, Karunadasa H, Cava R J, Mizel A and Schiffer P 2003 Phys. Rev. Lett. 91 107201
[45] Snyder J, Slusky J S, Cava R J and Schiffer P 2001 Nature 413 48
[46] Matsuhira K, Hinatsu Y and Sakakibara T 2001 J. Phys.: Condens. Matter 13 L737
[47] Snyder J, Ueland B G, Mizel A, Slusky J S, Karunadasa H, Cava R J and Schiffer P 2004 Phys. Rev. B 70 184431
[48] Xing H, He M, Feng C M, Guo H J, Zeng H and Xu Z A 2010 Phys. Rev. B 81 154426
[49] Henley C L 2010 Annu. Rev. Condens. Matter Phys. 1 179
[50] Arima T 2007 J. Phys. Soc. Jpn. 76 073702