# Electric control of magnetism in a multiferroic metal–organic framework

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Electric control of magnetism is demonstrated in a multiferroic metal–organic framework with a perovskite structure. A moderate electric field of a few kV/cm applied during the cooling process is able to cause a large (more than 50%) change of the magnetization at low temperature. This significant magnetoelectric effect is ascribed to the electric field manipulation of orientation of hydrogen bonds that modify the superexchange interaction between metal ions.
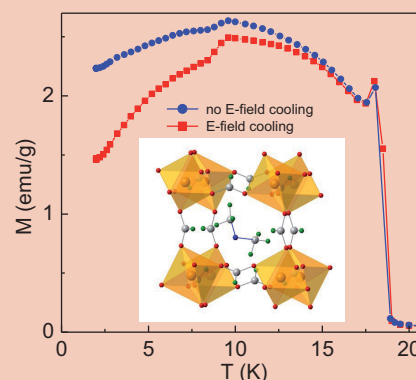


Electric-field cooling causes a large change in the magnetization of a multiferroic MOF.

**1 Introduction** Metal–organic frameworks (MOFs) consisting of networks of metal ions connected by coordinating organic linkers, have attracted considerable interest due to their great potential for applications in many fields, such as gas storage/separation, catalysis, nonlinear optics, photoluminescence, biomedical imaging, etc. [1–5]. More recently, the magnetic and electric properties of MOFs start to draw more attention because magnetic or ferroelectric/antiferroelectric orders can be achieved in specifically designed MOFs [6–10]. Especially, multiferroics in which magnetic and electric ordering coexist [11–13], a rare phenomenon in single-phase materials, has been discovered in a number of MOFs [14–16]. This opens up new routes to multiferroics beyond inorganic solids [17, 18]. In addition to multiferroics, the cross coupling between magnetic and electric orders, i.e., the magnetoelectric (ME) effects, is more important for practical applications. Our group recently reported an ME effect in the paramagnetic state of a MOF [19], which is not related to the low-temperature multiferroics and requires a high magnetic field. Nevertheless, the ME effects in the multiferroic state of MOFs have not been observed yet. This is probably due to the fact that the multiferroics in MOFs usually belong to the type-I multiferroics [20] where the magnetic and electric orders have separate origins. Thus, one may not expect a strong cross coupling between them. However, a recent theoretical study by Stroppa et al. suggests that a strong ME effect could be expected in certain multiferroic MOFs [21]. In this Letter, we demonstrate for the first time that a strong converse ME effect (electric control of magnetism) can be realized in a multiferroic MOF. A moderate electric field of a few kV/cm is able to cause a large change of the magnetization in the multiferroic state. This finding opens up a new strategy to electric control of magnetism.

**2 Sample and experiments** The MOF investigated in this work has a formula of $[(CH_3)_2NH_2]Fe(HCOO)_3$. It has a $ABX_3$ perovskite-like structure as shown in Fig. 1. The metal cations ($B = Fe^{2+}$) linked by the formate groups ($X = HCOO^-$) form the $BX_3$ skeleton, and the dimethyl-ammonium (DMA) cations ($A = [(CH_3)_2NH_2]^+$) occupy the cavities. The amine hydrogen atoms of $DMA^+$ can make hydrogen bonds with oxygen atoms of the formate groups. Previous studies on the isostructural MOFs have revealed that the $DMA^+$ cations are dynamically disordered at room temperature, but become cooperative ordering upon cooling due to the ordering of hydrogen bonding (N–H···O) [9, 22–24]. Just because of the disorder–order transition of hydrogen bonding, a ferroelectricity or antiferroelectricity could be induced.

Single crystal samples of the $[(CH_3)_2NH_2]Fe(HCOO)_3$ MOF were prepared by the solvothermal condition method. A 30 mL DMF solution containing 5 mmol metal chloride salts and 30 mL deionized water was heated in a poly-phenyl (PPL)-lined autoclaves for 3 days at 140 °C. The supernatants were transferred into a glass beaker to crystal-lization at room temperature, and cubic colorless crystals were obtained after 3 days. The crystals were filtered from the mother liquid and washed by ethanol. Powder X-ray diffraction (XRD) pattern at room temperature (see Supporting Information, Fig. S1) confirmed the structure and phase purity of the obtained samples. The single-crystal XRD pattern (Supporting Information, Fig. S1) suggests that the crystal is naturally grown along [012] direction. Magnetic properties were measured with a superconduct-ing quantum interference device magnetometer (Quantum Design MPMS). The dielectric constant was measured with a Agilent 4980 LCR meter in a Quantum Design physical properties 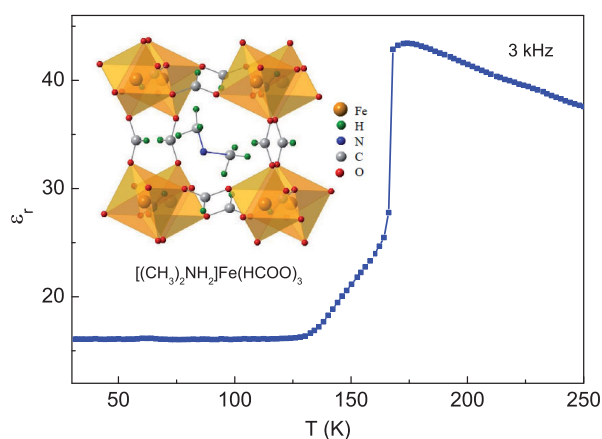measurement system (PPMS) using a home-made sample probe. All the measurements were per-formed along the [012] direction of a single crystal.

**3 Results and discussion** The dielectric constant of the MOF as a function of temperature is shown in Fig. 1. A sharp jump is observed at $T_C \sim 166$ K, followed by a slow decrease with increasing temperature. Similar to previous studies of other perovskite MOFs of $[(CH_3)_2NH_2]M(HCOO)_3$ with M = Zn and Mn [9, 14, 19], this dielectric anomaly signals a phase transition induced by the ordering of hydrogen bonding (N–H···O) upon cool-ing. The nature of this phase transition is still controversial. Both antiferroelectric and improper ferroelectric phase transition were proposed [9, 10]. We have measured the pyroelectric current across the phase transition, and a small electric polarization was obtained, indicating a weak ferro-electricity in the Fe-based MOF.

In addition to the dielectric ordering, this MOF also exhibits magnetic ordering at low temperature. Figure 2 presents the magnetization as a function of temperature measured after a zero-magnetic-field cooling (ZFC) proc-ess. Two magnetic transitions can be identified: one is at $T_N \sim 18$ K and another is around $T_B \sim 10$ K. The sharp transition at $T_N \sim 18$ K is due to a spin-canted antiferro-magnetic ordering, which is consistent with previous stud-



**Figure 1** Dielectric constant as a function of temperature meas-ured at 3 kHz. A dielectric transition due to the ordering of hydrogen bonding is observed at 166 K. The inset shows the $ABX_3$ perovskite-like structure of $[(CH_3)_2NH_2]Fe(HCOO)_3$ with $DMA^+$ in the cage. The two hydrogen atoms linked with nitrogen in $DMA^+$ forming hydrogen bonds were not added for clarity.
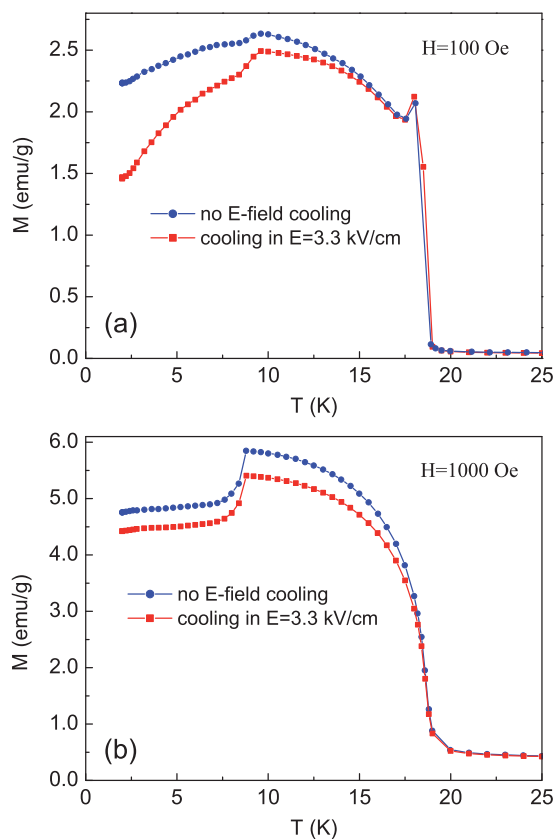


**Figure 2** Magnetization as a function of temperature with and without electric-field cooling, measured at (a) $H = 100$ Oe and (b) $H = 1000$ Oe.

Phys. Status Solidi RRL **8**, No. 1 (2014)

Rapid

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ies of isostructural MOFs containing Co and Ni, where the magnetic measurements on powder samples indicate a weak ferromagnetism induced by canted antiferromagnetic order [6]. A careful study of the low-temperature magnetic phase of the MOF suggests a magnetic phase separation in which canted antiferromagnetic order coexists with mononuclear $Fe^{2+}$ single-molecular magnets [25]. The drop of the ZFC magnetization below $T_B$ is due to the blocking of magnetic moments of $Fe^{2+}$ single-molecular magnets. A step-like hysteresis loop evidencing resonant quantum tunneling of magnetization has also been confirmed after subtracting the canted antiferromagnetic contribution [25].

Although the multiferroics has been well established in the perovskite MOFs, the ME effect in the multiferroic state has not been reported so far. We then investigated the influence of electric field on magnetism (the converse ME effect) by comparing the magnetization measured with and without electric-field cooling (EFC). The results are shown in Fig. 2. In all the measurements, the sample was cooled from 300 K to 2 K in zero magnetic field, and the magnetization was recorded with warming. The EFC experiments were performed as following: during the cooling process an electric field was applied along [012] at 200 K, which is above the disorder–order transition temperature ($\sim$166 K) of the hydrogen bonding; the electric field was removed at 2 K and the magnetization was measured at 100 Oe or 1000 Oe with warming.

A striking finding is that the magnetization in the multiferroic state is greatly influenced by the EFC process in a moderate electric field of 3.3 kV/cm. Below the magnetic ordering $T_N$, the magnetization measured after EFC is apparently smaller than that without EFC. The difference is more pronounced at low temperature in a low magnetic field. The ratio of magnetization change, defined as $R = \Delta M/M = [M(0) - M(E)]/M(E) \times 100\%$, is plotted in Fig. 3. At $H = 100$ Oe, the ratio of magnetization change increases with decreasing temperature, reaching 53% at 2 K. As far as we know, such a huge converse ME effect

has never been reported before. At $H = 1000$ Oe, the relative change of magnetization is less significant, with a ratio of $\sim$8% in the multiferroic state.

We believe that this significant ME effect is a consequence of electric field manipulation of orientation of hydrogen bonds. As described in Ref. [24], this MOF has an intrinsic magnetic phase separation due to the existence of two types of organic linkers between $Fe^{2+}$ ions: one is a pure formate group $HCOO^-$ and the other is a formate group coupled with the $DMA^+$ cation via a hydrogen bond (N–H···O). Therefore, there are two distinct superexchange paths in the MOF:

Fe–O–C–O–Fe    and    Fe–O–C–(O···HN)–Fe .

For the former, the superexchange between $Fe^{2+}$ ions leads to a canted antiferromagnetic order below $T_N \sim 18$ K. For the latter, the superexchange is greatly supressed because the geometry of superexchange path such as the bond angle and overlap between p- and d-orbitals has been dramatically altered when a hydrogen bond is inserted. As $Fe^{2+}$ in octahedral coordination of the perovskite structure has a relatively strong single-ion magnetic anisotropy [26], those $Fe^{2+}$ ions without superexchange interaction would behavior as mononuclear single-molecular magnets with a blocking temperature $T_B \sim 10$ K.

At high temperature, the hydrogen bonding is dynamically disordered. Upon cooling below $T_C \sim 166$ K, the hydrogen bonds start to become ordering. When an electric field is applied during cooling, the dipoles of hydrogen bonds tend to align along the direction of the electric field, which further strengthens the ordering of hydrogen bonding below $T_C$. As more hydrogen bonds are aligned along one direction, more superexchange paths are blocked by hydrogen bonding, and the proportion of $Fe^{2+}$ single-molecular magnets would increase. As a consequence, more magnetic moments are blocked at low temperature, which results in a significant reduction in magnetization.

**4 Summary** In summary, we have observed a large converse ME effect in the multiferroic MOFs, $[(CH_3)_2NH_2]Fe(HCOO)_3$. The magnetism in the multiferroic state can be effectively controlled by applying an electric field during the cooling process. A moderate electric field of 3.3 kV/cm is able to induce a huge change (more than 50%) in magnetization. We believe this pronounced ME effect is related to the alignment of hydrogen bonding manipulated by electric-field cooling. The correlation between hydrogen bond and magnetic ordering can be understood in terms of the influence of hydrogen bonding on the superexchange path (Fe–O–C–O–Fe). Our study not only presents the first example of strong ME effects in multiferroic MOFs, but also opens up a new strategy to electric control of magnetism via hydrogen-bond manipulation.
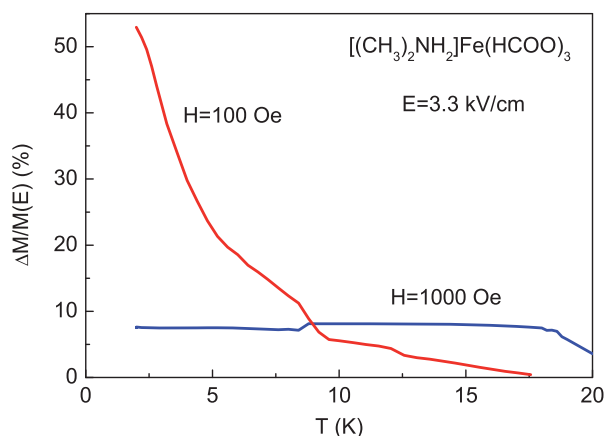
**Figure 3** Relative change of magnetization as a function of temperature after cooling in an electric field of 3.3 kV/cm.

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