

# The investigation of the magnetodielectric effect in multiferroic ferroelectromagnets

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**Abstract.** In multiferroic ferroelectromagnets, microscopic coupling interaction between the ferroelectric and magnetic order results in the macroscopic correlation between the dielectric and magnetic properties, which is defined as magnetodielectric effect. If we classify multiferroic ferroelectromagnets as two kinds: ferroelectric-ferromagnets and ferroelectric-antiferromagnets, we find the magnetodielectric behavior of these two kinds of ferroelectromagnets show obvious difference. We analyze the origin of the different magnetodielectric behavior and find that the fluctuation of the spin-pair correlation plays a critical role. Soft-mode theory based on DIFFOUR model and the mean-field theory are combined to deal with multiferroic ferroelectromagnetic system.

**PACS.** 77.80.-e Ferroelectricity and antiferroelectricity – 75.80.+q Magnetomechanical and magnetoelectric effects, magnetostriction – 77.22.-d Dielectric properties of solids and liquids

## 1 Introduction

Multiferroics are rare materials which show the coexistence of two or three of the ferroic orders: ferroelectric, (anti)ferromagnetic and ferroelastic in the same phase [1]. To our knowledge, the earliest discovery of Multiferroics were in the late 1950s and early 1960s, when the former Soviet union scientists found the hexagonal rare-earth manganites having the overall formula  $\text{RMnO}_3$  ( $R = \text{Y, Ho, Er, Tm, Yb, Lu or Sc}$ ), are ferroelectromagnets (FEM) with antiferromagnetic (AFM) and weak ferroelectric (FE) properties [2–7]. The discovery and development of FEM brings the era when the magnetic and ferroelectric properties are completely separated to an end. In theoretical aspect, the earliest work on magnetoelectric (ME) coupling can be traced back to 1959 [8], when Landau and Lifshitz predicted there was an allowed term in the free energy of the form  $\alpha_{i,j} H_i E_j$  based on the group theory, where  $E$  and  $H$  represent external electric and magnetic field,  $\alpha_{i,j}$  is the element of a tensor showing the correlation between  $H$  and  $E$ . Then Rado proposed the two-ion model and explained temperature dependence of the ME effect [9], followed by the ameliorated approaches of Hornreich et al. [10], Yatom et al. [11], and Gehring [12]. These theories, however, are concerned only with the coupling term caused by the external field as perturbation to the system, thus it is only applicable to the system which has weak coupling.

However, as far as FEM is concerned, although experimental evidence has shown that the ME energy, which comes from the coexistence of the spontaneous ferroelectric and antiferromagnetic order, can be comparable with the magnitudes of the intrinsic spin and ferroelectric energies [13, 14], it seems that this kind of ME energy does not trigger off research interest. One of the most important reasons is that, for many of the examined ferroelectromagnetic compounds, the ferroelectric transition temperature  $T_E$  is much higher than the magnetic transition temperature  $T_N$ . Intuitively, the coupling interaction will diminish as the difference between  $T_E$  and  $T_N$  increases. Thus such a coupling may not self-evident for ferroelectromagnets with  $T_E$  very different from  $T_N$ . Another reason arises from the difficulty in finding a suitable theory to describe the coupling. Besides, a measurable physical quantity hadn't been found to directly probe the magnetoelectric coupling. Until recently, Z.J. Huang et al. have detected an inversed S-shaped anomaly in both dielectric constant and loss tangent in bulk yttrium  $\text{YMnO}_3$  [15]. Detecting the ME coupling through the dielectric anomaly is a new method, which again ignites the interests in investigating the magnetoelectric effect in ferroelectromagnets. Subsequently, the similar dielectric anomaly has also been observed in other ferroelectromagnets, such as  $\text{BiMnO}_3$  [16],  $\text{EuTiO}_3$  [17],  $\text{TeCuO}_3$  and  $\text{SeCuO}_3$  [18] etc. Theoretically, Gao et al. [19, 20] first investigated the phase transition in ferroelectromagnetic lattice by the method of the Monte Carlo simulations. They proposed a possible coupling form to describe the intrinsic magnetoelectric coupling in the ferroelectromagnetic system and

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gave a detailed analysis of the magnetoelectric properties, which initiated the theoretical research on the inherent magnetoelectric coupling.

In the past two or three years, magnetocapacitance (MC), i.e. the change of the dielectric constant induced by the external magnetic field, becomes a hot issue. Large magnetocapacitance has been observed in ferroelectromagnets BiMnO<sub>3</sub> [16], EuTiO<sub>3</sub> [17], SeCuO<sub>3</sub> [18], DyMnO<sub>3</sub> [21] etc. On the one hand, the measurement of the magnetocapacitance is a powerful technique to detect the magnetoelectric coupling mechanism. On the other hand, MC itself is attractive for practical applications. A number of device applications have been suggested for the magnetodielectric effect, including multiple state memory elements, electric field controlled ferromagnetic resonance device, and variable transducers with either magnetically modulated piezoelectricity or electrically modulated piezomagnetism.

In this paper, we define the magnetic influence on the dielectric property as magnetodielectric (MD) effect. Considering the different magnetic property between ferromagnet and antiferromagnet, we classify FEM as the ferroelectric-ferromagnets (FE-FM) and ferroelectric-antiferromagnets (FE-AFM). The magnetodielectric effect in FE-FM and FE-AFM is given a comparative investigation from three aspects: 1. The origin of the MD effect; 2. The dielectric change; 3. The magnetoelectric susceptibility.

## 2 Models and analysis

In our model, we divide the ferroelectromagnetic system into two separated subsystems: the magnetic subsystem and the ferroelectric subsystem. Meanwhile, we introduce the coupling form as a medium to connect the two subsystems. Following Alcantara and Gehring [22] and Janssen [23], the Hamiltonian can be written in three parts as follows:

$$H = H^m + H^e + H^{me}, \quad (1)$$

where  $H^m$ : the Hamiltonian of the magnetic subsystem,  $H^e$ : the Hamiltonian of the ferroelectric subsystem, and  $H^{me}$ : the coupling between the two subsystems.

Ising model is used to describe the magnetic subsystem. The Hamiltonian of the magnetic subsystem  $H^m$  comprises four origins: the coupling of the nearest neighbors and the next nearest neighbors, magnetic static energy, and single-ion anisotropy energy

$$H^m = - \sum_{\langle i,j \rangle} J_1 S_i S_j - \sum_{[k,l]} J_2 S_k S_l - \sum_i h S_i - D \sum_i S_i^2. \quad (2)$$

$J_1$  and  $J_2$  represent the nearest and next nearest exchange integral, respectively.  $h$  is the external magnetic field along spin ordered direction.  $D$  indicates the uniaxial single-ion anisotropy constant.  $S_i$  is the Ising spin at site  $i$  (the total spin quantum number  $S = 2$ ).  $\langle i, j \rangle$  and  $[k, l]$  denote that over the nearest and the next nearest neighbors are summed once, respectively.

The Hamiltonian of the ferroelectric subsystem  $H^e$  is composed of three parts, the first part is the kinetic and potential energy of the particle, which we use DIFFOUR model to describe [23]. The DIFFOUR model includes a potential energy term and the enharmonic potential, which is called a double-well potential. The second is the nearest neighbor electric interaction, and the third is electric static energy

$$H^e = \sum_i \left( \frac{p_i^2}{2m} - \frac{a}{2} u_i^2 + \frac{b}{4} u_i^4 \right) - \sum_{\langle i,j \rangle} U u_i u_j - \sum_i E u_i. \quad (3)$$

$m$  is the mass.  $p_i$  and  $u_i$  are the particle momentum and the electric displacement at site  $i$ , respectively.  $a$  and  $b$  represent the double-well potential parameters.  $U$  indicates polarization interaction coupling parameter, and  $E$  denotes external electric field, which is parallel to the polarization direction.  $\langle i, j \rangle$  represents that over the nearest neighbors is summed once.

For the coupling interaction between the two subsystems, we introduce the coupling mechanism proposed by Gao et al., which has been pointed out in the previous section

$$H^{me} = \sum_{\langle k,i \rangle, \langle k,j \rangle} \varepsilon_{ij} g u_k^2 S_i S_j, \quad (4)$$

where  $g$  is the magnetoelectric coupling coefficient indicating the intensity of the magnetoelectric coupling,  $u_k$  is the electric displacement at site  $k$ ,  $i$  and  $j$  are the nearest neighbor of site  $k$ , but  $i$  and  $j$  are different sites. For ferromagnetic structure,  $\varepsilon_{ij} = 1$ . For antiferromagnetic structure, we adopt the same definition of  $\varepsilon_{ij}$  as Gao's paper.

When we aim at investigating the dielectric properties of the ferroelectromagnetic system. The Hamiltonian, under the mean-field approximation, can be expressed as the following:

$$H = H^E + C_1, \quad H^E = H^e + H^{me}, \quad (5)$$

$$H^E = \sum_i \left( \frac{p_i^2}{2m} - \frac{\tilde{a}}{2} u_i^2 + \frac{b}{4} u_i^4 \right) - \tilde{E} \sum_i u_i, \quad (6)$$

$$\tilde{E} = E + U z_1 p, \quad (7)$$

$$\tilde{a} = a - 2z_2 g \langle S_i S_j \rangle, \quad (8)$$

where  $C_1$  is a constant, representing the contribution of the magnetic part  $H^m$ .  $\tilde{E}$  is the effective mean-field acting on the ferroelectric subsystem.  $\tilde{a}$  represents the amended double-well potential parameter.  $u_i$  is proportional to the local spontaneous polarization  $p$ , i.e.  $p = \langle u_i \rangle$ .  $\langle \dots \rangle$  represents the thermal average of the corresponding physical quantities, therefore, thus  $\langle S_i S_j \rangle$  is the average value of the spin-pair correlation. In cubic crystal,  $z_1 = 6$  is the nearest-neighbor number of ferroelectric particles to a given ferroelectric particle.  $z_2 = 12$  is the number of the spin-pair correlation that will directly influence a given ferroelectric particle.

Equations about polarization and the dielectric constant can be obtained from the soft-mode theory

$$(-\tilde{a} + 3b\sigma + bp^2)p = z_1Up + E, \quad (9)$$

$$\sigma(-\tilde{a} + 3b(\sigma + p^2)) = k_B T, \quad (10)$$

$$\varepsilon(h, T) = \frac{\partial p}{\partial E} = \frac{1}{-\tilde{a} + 3b(\sigma + p^2) - z_1U}, \quad (11)$$

$$\chi_{em} = \frac{\partial p}{\partial h}, \quad (12)$$

where  $\sigma$  is the fluctuation of the electric displacement, i.e.,  $\langle u_i^2 \rangle = \langle u_i \rangle^2 + \sigma$ ,  $\varepsilon(h, T)$  represents the actual dielectric constant if we neglect the vacuum dielectric constant.  $\chi_{em}$  is the magnetoelectric susceptibility. Obviously, due to the presence of the magnetoelectric coupling both the polarization  $p$  and the dielectric constant  $\varepsilon$  are the function of spin-pair correlation  $\langle S_i S_j \rangle$ . Here when we expand equation (15) to the linear term of  $\langle S_i S_j \rangle$ ,  $\varepsilon(h, T)$  can be approximately rewritten as

$$\varepsilon(h, T) = \varepsilon_0(1 + \gamma \langle S_i S_j \rangle), \quad (13)$$

where  $\varepsilon_0 = \frac{1}{-a+3b(\sigma_0+p_0^2)-z_1U}$  is the dielectric constant in the absence of the ME coupling, and  $\gamma = 2z_2g\varepsilon_0$  is taken as a normalized magnetoelectric coupling factor.

In order to ascertain the magnetic influence on the dielectric property, we need to investigate the fluctuation of the spin-pair correlation. The Hamiltonian of the ferroelectromagnets can be rewritten as the following:

$$H = H^M + C_2, \quad H^M = H^m + H^{me}, \quad (14)$$

where  $C_2$  is a constant, representing the contribution of the electric part  $H^e$ .

For FE-FM, the calculation procedure about the spin-pair correlation is listed in the following:

$$\begin{aligned} H^M &= - \sum_{\langle i,j \rangle} \tilde{J}_1 S_i S_j - \sum_{[l,k]} J_2 S_l S_k - \sum_i h S_i - D \sum_i S_i^2 \\ &= - \sum_i \tilde{h} S_i - D \sum_i S_i^2 \end{aligned} \quad (15)$$

$$\tilde{h} = z_1 \tilde{J}_1 \langle S \rangle + z_2 J_2 \langle S \rangle + h, \quad (16)$$

$$\tilde{J}_1 = J_1 - z_3 g p^2, \quad (17)$$

where  $\tilde{h}$  is the effective mean-field acting on the magnetic subsystem,  $\tilde{J}_1$  represents the amended exchange integral,  $\langle S \rangle$  is the average value of the expectation value of the Ising spin,  $z_3 = 4$  is the number of the ferroelectric particle that will directly influence a given spin-pair correlation. Then using the thermodynamic statistics, we derive the average value of the spin-pair correlation in the following:

$$\begin{aligned} \langle S \rangle &= \frac{\text{Tr} \left[ S_i \exp \left[ -\beta \left( -\tilde{h} \sum_i S_i - D \sum_i S_i^2 \right) \right] \right]}{\text{Tr} \left[ \exp \left[ -\beta \left( -\tilde{h} \sum_i S_i - D \sum_i S_i^2 \right) \right] \right]} \\ &= \frac{4e^{4\beta D} \sinh(2\beta\tilde{h}) + 2e^{\beta D} \sinh(\beta\tilde{h})}{1 + 2e^{4\beta D} \cosh(2\beta\tilde{h}) + 2e^{\beta D} \cosh(\beta\tilde{h})}, \end{aligned} \quad (18)$$

$$\langle S_i S_j \rangle \approx \langle S \rangle^2, \quad (19)$$

where  $\beta = \frac{1}{k_B T}$ ,  $\sinh(x)$  and  $\cosh(x)$  are the hyperbolic cosine function. With the approximation in equation (23), the fluctuation of the spin-pair correlation induced by the external magnetic field can be expressed as:  $\Delta \langle S \rangle^2 = \langle S \rangle_{(h,T)}^2 - \langle S \rangle_{(0,T)}^2$ .

For FE-AFM, to calculate the spin-pair correlation, we divide the magnetic subsystem into two sublattices  $a$  and  $b$

$$\begin{aligned} H^M &= - \sum_{\langle i,j \rangle} \tilde{J}_1 S_i S_j - \sum_{[l,k]} J_2 S_l S_k - \sum_i h S_i - D \sum_i S_i^2 \\ &= - \sum_i \tilde{h}_a S_{ai} - D \sum_i S_{ai}^2 - \sum_j \tilde{h}_b S_{bj} - D \sum_j S_{bj}^2, \end{aligned} \quad (20)$$

$$\tilde{h}_a = z_1 J_1 \langle S_b \rangle + z_2 J_{2a} \langle S_a \rangle + h, \quad (21)$$

$$\tilde{h}_b = z_1 J_1 \langle S_a \rangle + z_2 J_{2b} \langle S_b \rangle + h, \quad (22)$$

$$J_{2a} = J_2 + 2gp^2, \quad J_{2b} = J_2 - 2gp^2, \quad (23)$$

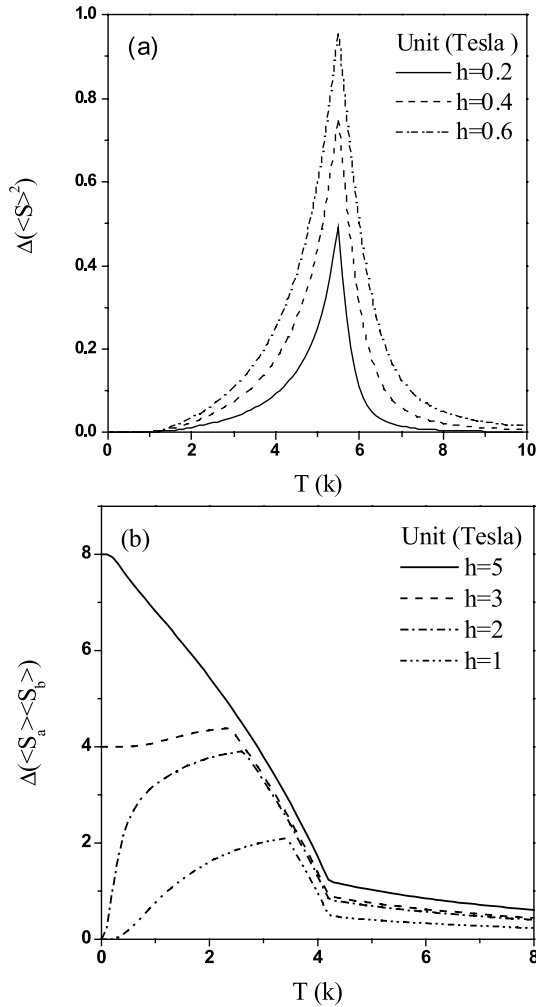
$$\langle S_i S_j \rangle \approx \langle S_a \rangle \langle S_b \rangle. \quad (24)$$

$\langle S_a \rangle$  and  $\langle S_b \rangle$  are the sublattice magnetization which can be obtained by the same method in equation (18).  $\tilde{h}_a$  and  $\tilde{h}_b$  are the mean-field acting on the two sublattices  $a$  and  $b$ , respectively.  $J_{2a}$  and  $J_{2b}$  are the amended exchange integrals. With the approximation of equation (28), the fluctuation of the spin-pair correlation induced by the external magnetic field can be expressed as:  $\Delta(\langle S_a \rangle \langle S_b \rangle) = (\langle S_a \rangle \langle S_b \rangle)_{(h,T)} - (\langle S_a \rangle \langle S_b \rangle)_{(0,T)}$ .

### 3 Results and discussion

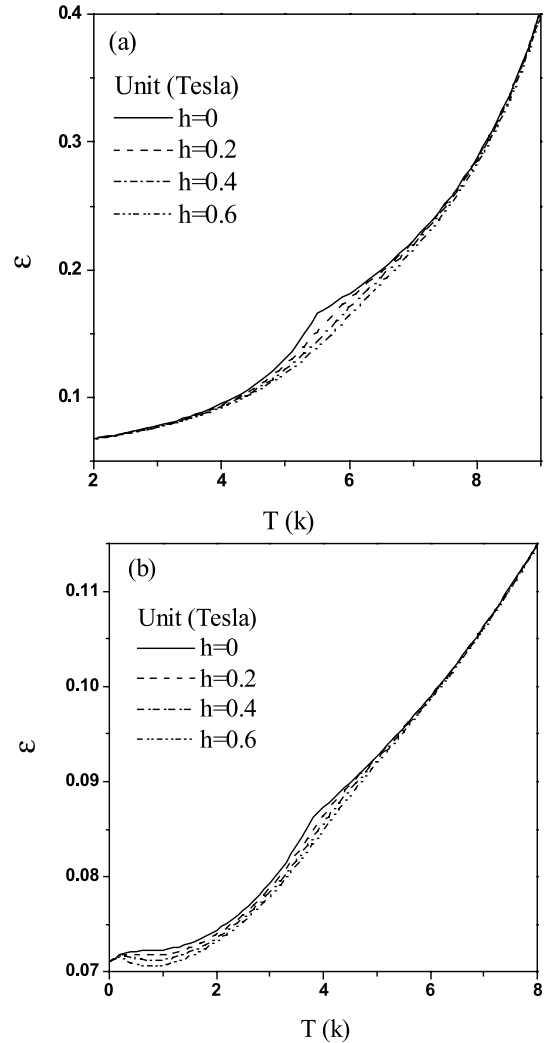
Parameters used in our paper don't contrapose a given ferroelectromagnet. They are representative of the family of ferroelectromagnets for qualitative research. For ferroelectric subsystem, we choose  $a = 2$ ,  $b = 4$  to produce the spontaneous ferroelectric order. For magnetic subsystem we choose  $J_1 = 0.25$  (or  $J_1 = -0.25$ ),  $J_2 = 0.03$ ,  $D = 0.05$  to produce the ferromagnetic (or antiferromagnetic) order. The magnetoelectric coupling coefficient is given a moderate value:  $g = -0.012$ . According to the given parameters, we get the ferroelectric transition temperature:  $T_E = 18$  K, and magnetic transition temperature:  $T_C = 5.4$  K for FE-FM,  $T_N = 3.9$  K for FE-AFM. This fits the fact that in most ferroelectromagnets  $T_N$  (or  $T_C$ )  $< T_E$ .

From the theoretical analysis we know that the anomaly of the dielectric property, stemming from the ME coupling, is closely related with the spin-pair correlation. Therefore, we first discuss the fluctuation of the spin-pair correlation. Thermal excitation and external magnetic field are two important factors that affect the fluctuation. Figure 1a displays temperature dependence of the fluctuation for FE-FM, in which the magnetic fields are given as 0, 0.2, 0.4, 0.6 (tesla). Under a



**Fig. 1.** FE-FM: Temperature dependence of the spin-pair correlation fluctuation  $\Delta(\langle S^2 \rangle)$  under different magnetic fields  $h = 0.2, 0.4, 0.6$  (tesla); (b) FE-AFM: Temperature dependence of the spin-pair correlation fluctuation  $\Delta(\langle S_a \rangle \langle S_b \rangle)$  under the magnetic fields  $h = 1, 2, 3, 5$  (tesla).

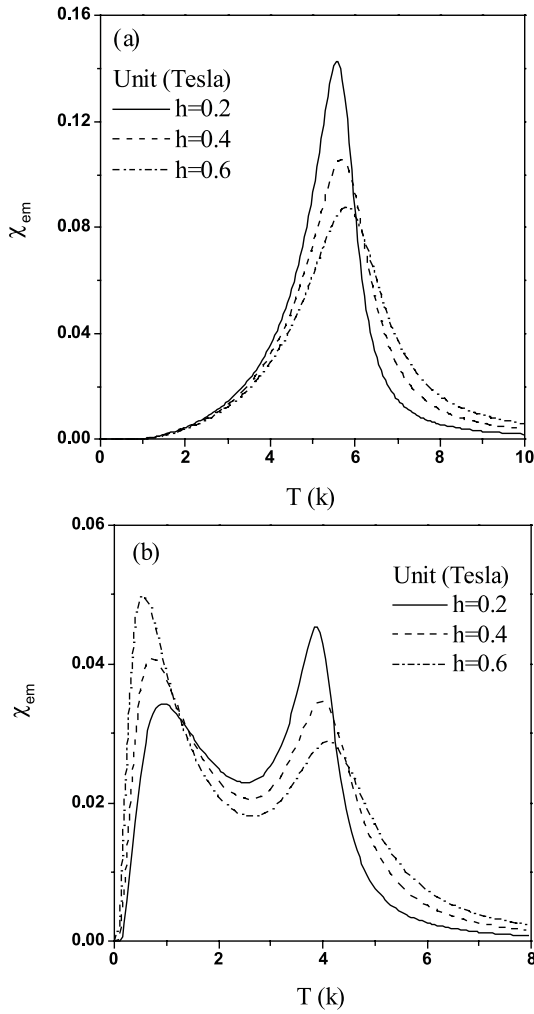
fixed magnetic field background, fluctuation has its maximal value around the magnetic transition temperature  $T_C$ , away from which the fluctuation will soon decrease. Under a fixed temperature background, a higher magnetic field will induce a larger fluctuation. Figure 1b provides the case of FE-AFM. The magnetic fields are given a large range from 1 to 5 (tesla) to thoroughly see the fluctuation of the spin-pair correlation. As we can see, with the increasing magnetic fields, the spin-pair correlation below  $T_N$  undergoes a remarkable change. The different phenomena between FE-FM and FE-AFM may be easily understood. For antiferromagnet, a larger magnetic field can completely destroy the antiferromagnetic phase and force the ferromagnetic phase, which means that the spin-pair correlation undergoes a qualitative change from the antiferromagnetic coupling to ferromagnetic coupling. While for ferromagnet, only around the magnetic transition temperature  $T_C$  the spin-pair correlation may undergo an



**Fig. 2.** FE-FM: Temperature dependence of the dielectric constant under  $\epsilon$  different magnetic fields  $h = 0.2, 0.4, 0.6$  (tesla); (b) FE-AFM: Temperature dependence of the dielectric constant  $\epsilon$  under different magnetic fields  $h = 0.2, 0.4, 0.6$  (tesla).

appreciable change from disordered phase to ferromagnetic coupling.

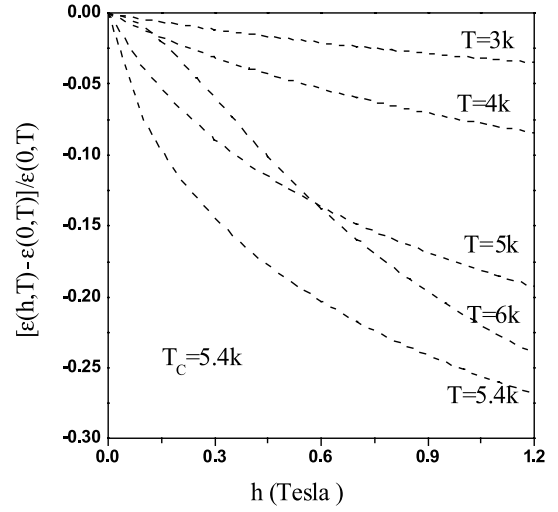
The dielectric diagram of FE-FM is shown in Figure 2a. There are three attracting phenomena in Figure 2a. First, when the applied magnetic field is absent (i.e.  $h = 0$ ),  $\epsilon$  has a distinct anomaly at  $T_C$  for the onset of the spontaneous magnetic order. Second, both  $\epsilon$  and the anomaly of are suppressed for the application of the magnetic fields, and the suppression becomes larger with the increasing magnetic fields. As we know, with the application of the magnetic field, the spin-pair experiences a continuous transition from paramagnetic to ferromagnetic phase. This explains why the dielectric anomaly is suppressed. Third, only around  $T_C$ , the suppression of  $\epsilon$  induced by the external magnetic fields is remarkable. All these phenomena support one fact: for FE-FM, temperature around  $T_C$  and large magnetic field are two necessary conditions to obtain remarkable dielectric change.



**Fig. 3.** FE-FM: Temperature dependence of the magnetoelectric susceptibility  $\chi_{em}$  under different magnetic fields  $h = 0.2, 0.4, 0.6$  (tesla); (b) FE-AFM: Temperature dependence of the magnetoelectric susceptibility  $\chi_{em}$  under different magnetic fields  $h = 0.2, 0.4, 0.6$  (tesla).

In Figure 2b, temperature dependence of the dielectric constant of FE-AFM is drawn. Compare Figure 2a with Figure 2b, we find that the dielectric constant of FE-FM and FE-AFM shows the similar characters around their respective magnetic phase transition temperature. That is to say, the three phenomena mentioned above also appear in FE-AFM. What makes difference is that, in FE-AFM the dielectric change induced by external magnetic field exists throughout the temperature range below  $T_N$ . This is attributed to the spin-pair fluctuation of FE-AFM.

$\chi_{em}$  obtained from equation (12) indicates the dielectric response to external magnetic field, which we call the magnetodielectric response. As we can imagine, if no magnetoelectric coupling exists,  $\chi_{em}$  must be zero, therefore, nonzero  $\chi_{em}$  can be regarded as a unique property for FEM. In Figure 3a, we plot temperature dependence of  $\chi_{em}$  for FE-FM. This figure conveys two pieces of important information. First, as a function of



**Fig. 4.** Magnetic-field dependence of magnetocapacitance  $\frac{\epsilon(h,T) - \epsilon(0,T)}{\epsilon(0,T)}$  at different temperatures.

the temperature,  $\chi_{em}$  has its maximal value at  $T_C$ . This demonstrates that the most remarkable magnetodielectric effect appears around  $T_C$ . When temperature departs from  $T_C$ ,  $\chi_{em}$  decreases fast, showing the fading of the magnetodielectric effect. Second, if we compare the three curves which correspond to  $h = 0.2, 0.4, 0.6$  (tesla), respectively, we find a higher magnetic field will induce a lower, smoother and broader peak. When  $h$  approaches to zero, the peak is divergent (we haven't shown it) corresponding to the anomaly in Figure 2a. The lowering trend of the peak-value means that, the magnetodielectric response decreases with the increasing magnetic field. In Figure 3b, the magnetoelectric susceptibility diagram of FE-AFM is provided, in which two peaks are observed: one is around  $T_N$ , and the other is below  $T_N$ . We can see that the low-temperature peak increases with the increasing magnetic field, which is contrary to the behavior of the peak at  $T_N$ . We find that when the applied magnetic field is low, the magnetodielectric response at  $T_N$  dominates. When the magnetic field gets higher, the low-temperature response gets to the windward. If we continue to increase the magnetic field, the peak at  $T_N$  will be completely suppressed and the low-temperature peak will shift to  $0$  K (not shown). In sum, for FE-AFM, higher magnetic field and low temperature are two necessary conditions to obtain larger magnetocapacitance and magnetodielectric response.

In the end, we specially investigate the magnetocapacitance for FEM-FM in Figure 4. We can see that the MC-curve shows a steep decrease in the low-field range. When the applied magnetic field becomes higher, the trend of the curve becomes flat. What's more, when the external magnetic field is high enough, MC gets to its saturated value. From the slope of the curve we draw the same conclusion in Figure 3a: the dielectric response decreases with the increasing magnetic field. In addition, compare the magnetocapacitance at different temperatures, we find that the absolute magnitude of the magnetocapacitance increases with the increasing temperature and gets to the

maximum around  $T_C$  ( $T_C \approx 5.4$ ). If we further increase the temperature to make the system enter into the paramagnetic phase, we find that the magnetocapacitance again decreases. This is in good agreement with the experimental result [16].

## 4 Conclusion

In the present work, we investigate the magnetodielectric effect in ferroelectromagnets from three aspects: 1. Origin of the magnetodielectric effect; 2. dielectric change; 3. Magnetodielectric response. For ferroelectric-ferromagnets, large magnetocapacitance and magnetodielectric response are observed only around  $T_C$ . When temperature is away from  $T_C$ , they soon diminish. In addition, we find the magnetocapacitance increases with the increasing magnetic field, while the magnetodielectric response decreases with the increasing magnetic field. For ferroelectric-antiferromagnets, low-temperature range draws our attention. With the application of a higher magnetic field, both large magnetocapacitance and magnetodielectric response are observed in low-temperature range. The practical interest in multiferroic ferroelectromagnets arises from device applications. As a qualitative research, our theoretical work may provide helpful guidance for the practical application.

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