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Coupling between the magnetism and dielectric properties in $Eu_{1-x}Ba_xTiO_3$

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The dielectric constant of the quantum paraelectric $EuTiO_3$ exhibits a sharp decrease at about 5.5 K, at which temperature antiferromagnetic ordering of the Eu spins simultaneously appears, indicating coupling between the magnetism and dielectric properties. A similar feature has also been detected in $Eu_{1-x}Ba_xTiO_3$ $(0<x\leqslant 0.2)$. The random-bond model within the framework of the transverse-field Ising model and the site dilution model based on the Heisenberg model are successfully applied to the $Eu_{1-x}Ba_xTiO_3$ electrical and magnetic subsystems, respectively. By adding an appropriate coupling term between the magnetic and electrical subsystems, which is related to the interaction of the Heisenberg spin and pseudospin, we investigate intrinsic coupling between the magnetic and electrical subsystems and successfully obtain its special dielectric constant, which is in good agreement with the experimental data.

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I. INTRODUCTION

Various interesting phenomena such as colossal magnetoresistance in perovskite manganites are produced through coupling between magnetism and transport properties in metals. Correspondingly, it is desirable that there exists coupling between magnetism and dielectric properties in certain magnetic insulators, where the dielectric properties are affected by the localized spins. In yttrium manganite $YMnO_3$, for one example, an inverse S-shaped anomaly in both dielectric constant and loss tangent is detected near its magnetic ordering temperature, which is the contribution of the frustration on the triangular lattice.[1–3] For another example, $EuTiO_3$ with the crystal structure presented in Ref. 4, it has been reported[4] recently that the dielectric constant shows an evident anomaly at its Néel temperature T_N, indicating coupling between magnetism and dielectric properties.

The previous research on $EuTiO_3$ mainly reveals its magnetic properties. A neutron-diffraction study[5] of $EuTiO_3$ indicates that a type-G antiferromagnetic structure exists, i.e., the six nearest-neighbor Eu ions to a given Eu ion have opposite spins while the 12 next-nearest-neighbor Eu ions have parallel spins. Shafer[6] pointed out that Eu ion has stable electron configuration $(S=7/2)$, which is completely different from the most of the perovskite titanates $R\mathrm{TiO}_3$ (R=rare earth), where both R and Ti are trivalent. That is to say, $EuTiO_3$ has a magnetic divalent Eu and accordingly a tetravalent Ti. But the recent observation on $EuTiO_3$ reveals its special dielectric properties,[4] which leads us to pay attention to coupling between its magnetic and electrical subsystems.

X-ray-absorption near-edge structure[7] has shown that both $EuTiO_3$ and $SrTiO_3$ exhibit no lattice distortion from the ideal perovskite structure, from which one may speculate that $EuTiO_3$ is similar to $SrTiO_3$ as a quantum paraelectric demonstrating no frequency dispersion, which is testified through dielectric measurements.[4] Due to the stabilization of the paraelectric phase by the quantum fluctuations,[8] the dielectric constant of quantum paraelectrics is so different from that of the normal ferroelectrics that it increases with decreasing temperature, gradually deviating from the Curie-Weiss law, and saturates at a very low temperature. But $EuTiO_3$ is a special quantum paraelectric, in which the dielectric constant shows a sharp decrease at its T_N, while it follows the feature of normal quantum paraelectric above T_N. Furthermore the dielectric constant of $EuTiO_3$ exhibits similar behavior to the calculated spin correlation $\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle$ between the nearest-neighbors Eu spins. Thus it is enlightening to consider the possible coupling mechanism between the magnetic and electrical subsystems at low temperatures.

In this paper, we focus on $Eu_{1-x}Ba_xTiO_3$ $(0\leqslant x\leqslant 0.2)$, which can be regarded as not only a quantum paraelectric containing impurities[9–15] just as $Sr_{1-x}Ba_xTiO_3$ or $Sr_{1-x}Ca_xTiO_3$, but also an antiferromagnet doped with impurities. It should be noted that our previous treatment[16] of coupling effect on the dielectric constant and soft-phonon mode in pure $EuTiO_3$ within the framework of the soft-mode theory cannot be employed for the impurity-doped cases. Other ways have to be found to solve this problem.

It is generally accepted that the order-disorder behavior becomes important near the perovskite ferroelectrics cubic-tetragonal phase transition because of the existence of multisite potential structure. Therefore, an order-disorder model can well explain their ferroelectric phase transition. A good example is $BaTiO_3$, in which it is believed[17] that the presence of polar clusters above the phase-transition temperature is linked with the crossover from the displacive to the order-disorder limit, which is testified by the experimental observation of a strong relaxation in the frequency range 10^8–10^9 Hz,[18] and the order-disorder behavior plays an important role. The transverse-field Ising model (TIM), which successfully treats the interaction of the dipolar moments through the pseudospin interaction term as well as the quantum-mechanical effects through the term including tunneling frequency within a unified framework,[19–21] can well describe the ferroelectric phase transition in $BaTiO_3$. As far as the quantum paraelectrics are concerned, the TIM has been used extensively and successfully to study both the pure quantum paraelectrics and their impurity-doped cases because of its advantages in explaining the decisive quantum effect in the quantum paraelectrics.[19,22,23] Therefore, it is enlightening to use the TIM to treat $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.2)$ to obtain good estimation of this system directly from the information available on the pure materials EuTiO_3 and BaTiO_3 by averaging some key quantities. The electrical subsystem of the doped quantum paraelectric is studied by using random-bond model within the framework of the TIM. As for the magnetic subsystem, we use the site-dilution model based on the Heisenberg model to study the antiferromagnetic properties. It should be noted that similar numerical calculation has been carried out on the related system of $\mathrm{Sr}_{1-x}\mathrm{Ca}_x\mathrm{TiO}_3$.[19,20,24–27] In order to explain anomalies occurring at $x > 0.1$, the lattice collapse due to the small Ca^{2+} ion was accounted for by piezoelectric coupling.[25] In the present study on $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.2)$, similar effects due to the lattice expansion by doping with large Ba^{2+} ions are taken into account by corrections to the pseudospin density (see below).

It is well known that there exist some interesting phenomena when the pure quantum paraelectrics are doped with small content of impurities. Because quantum paraelectrics can be classified as marginal systems at the limit of their paraelectric phase stability, small perturbation from impurities may destroy such stability. It has been found that SrTiO_3 crystal doped with Ba^{2+}, Pb^{2+}, and Ca^{2+} shows a ferroelectric phase transition with the transition temperature proportional to $(x - x_c)^{1/2}$,[10] where x is the impurity molar concentration and x_c is the critical concentration (quantum limit). For $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$, the calculated critical concentration is about 0.24, which is significantly larger than that of $\mathrm{Sr}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ and $\mathrm{Sr}_{1-x}\mathrm{Ca}_x\mathrm{TiO}_3$. So the ferroelectric phase transition mentioned above will not occur in $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.2)$, and its dielectric properties may be similar to those shown in Ref. 17 for the case $x < x_c$. That is, if the coupling interaction between the magnetism and dielectric properties is not taken into account, the dielectric constant of $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.2)$ will not peak evidently with the variation of temperatures, but its magnitude will increase with the impurity content. Above all, the dielectric constant shows anomaly at low temperatures because the coupling interaction actually exists in this system.

In spite of the experimental success in observing the dielectric anomalies in some ferroelectromagnets and quantum paraelectrics,[4,28,29] the nature of the coupling mechanism and the form of the interaction is still a debated issue. Experimental evidence shows that the energy of the coupling interaction is comparable with the magnitudes of the inherent spin and ferroelectric energies.[30,31] Accordingly, the energy of coupling must be involved in the system Hamiltonian. Gao *et al.*[32] utilized Monte Carlo simulations on the basis of the Ising-DIFFOUR model[33] to investigate the phase transition in the two-dimensional ferroelectromagnetic lattice, where the spin moment and polarization interact. For $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$, however, things are different. First, pure EuTiO_3 is a typical example where the Heisenberg model applies instead of the Ising model, since the magnetic ions are in an *s*-type orbital and the exchange interaction is isotropic. Second, based on available experimental data for $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$, Katsufuji and Takagi[4] suggested that the dielectric constant and spin correlation of the nearest neighbors $\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle$ were related as $\varepsilon(g) = \varepsilon(0)(1 + \alpha\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle)$. For pure EuTiO_3 this relation has been proved in our previous work.[9] Thus for the impurity-doped cases, it is reasonable to add a term in the Hamiltonian with the form of $-g\sum_{\langle i,j\rangle}\sum_{k,l}\sigma_k^z\sigma_l^z\vec{S}_i \cdot \vec{S}_j\theta_i C_j$ to describe the coupling interaction between the electrical and magnetic subsystems, where σ_k^z is the pseudospin equivalent to the polarization of the electrical subsystem and is used to scale the degree of ordering. There is another important aspect that should be considered: similar to triglycine sulfate,[34,35] where the alanine impurities can cause a strong internal bias field in the crystal lattice, the Ba impurities may cause a strong intrinsic frozen field, which is represented by E_0 in the present paper, and this field may increase with the impurity content.[21] So in $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$, the intrinsic field-induced polarization should be found. Therefore, it is desirable that the spin moment and this polarization interact with each other via the coupling term mentioned above.

In the present paper, we not only obtain the relation between the dielectric constant and the spin correlation in $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$, which is in good agreement with the experimental result, but also get the analytical relations between the polarization and the spin correlation $\langle\langle P \rangle\rangle(g) = \langle\langle P \rangle\rangle(0)(1 + \beta\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle)$, which makes the dielectric behavior more comprehensible. Furthermore, the spin correlation and Néel temperature vary at the same time due to the coupling interaction especially for higher impurity content according to our calculation.

II. MODELS AND ANALYSIS

We concentrate on $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.2)$ and consider the Hamiltonian for a three-dimensional cubic system with periodic boundary conditions. Two parameters S_i and σ_k are introduced here to represent the Heisenberg spin at Eu site and the pseudospin for the electrical subsystem, respectively. In addition, the coupling interaction between the electrical and magnetic subsystems is taken into account. So the Hamiltonian for this system can be presented as following:

$$H = H^e + H^m + H^{me}, \tag{1}$$

where H^e denotes the Hamiltonian for the diluted electrical subsystem, H^m is the Hamiltonian for the diluted magnetic subsystem, and H^{me} is the coupling interaction between the two subsystems.

As mentioned in the Introduction, the TIM, in which the pseudospin interaction represents the interaction of the dipolar moments and the tunneling frequency embodies the quantum effect, can well describe the quantum effect in quantum paraelectrics as well as the ferroelectric phase transition in ferroelectrics. As a result, the diluted electrical subsystem of $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.2)$ can be treated within the framework of the TIM, and H^e in the presence of electric field can be written as following:

$$H^e = -\Omega \sum_k \sigma_k^x - \frac{1}{2} \sum_{k,l} J_{k,l} \sigma_k^z \sigma_l^z - 2\mu \sum_k (E_0 + E) \sigma_k^z, \tag{2}$$

where $k \neq l$, $\sigma_k = \frac{1}{2}$ and $-\frac{1}{2}$ for up and down pseudospins, E represents the external electric field, μ is the effective dipole moment of each pseudospin, $J_{k,l}$ denotes the nearest-neighbor pseudospin interaction, the summation $\Sigma_l J_{k,l} = J$ covers the nearest neighbors of site k , Ω is the tunneling frequency, and E_0 represents the intrinsic frozen field caused by impurity doping. It should be noted that the parameters J, Ω, and μ are supposed to follow the double-peak distribution to deal with the impurity content. In this system, the mean electrical polarization is proportional to the z component of the pseudospins introduced in the TIM.

It is well known that for pure $EuTiO_3$ the magnetic interaction between Eu $4f$ spins originates from (i) superexchange (antiferromagnetic) through the O $2p$ state and also from (ii) indirect exchange through the Eu $5d$ state. For the reason that the exchange interaction in $EuTiO_3$ is isotropic, as is mentioned in Introduction, we employ the site-dilution model within the framework of Heisenberg model to describe the Hamiltonian of $Eu_{1-x}Ba_xTiO_3$ magnetic system on the basis of pure $EuTiO_3$. Therefore, when the impurity effect is taken into account, H^m for $S = 7/2$ can be written as

$$H^m = \sum_{\langle i,j \rangle} A_1 \vec{S}_i \cdot \vec{S}_j \theta_i C_j + \sum_{[i,j]} A_2 \vec{S}_i \cdot \vec{S}_j \theta_i C_j - \sum_i \vec{h} \cdot \vec{S}_i \theta_i, \tag{3}$$

where $\vec{S}_i$ is the Heisenberg spin at Eu site i, and the exchange integrals $A_1 = 0.037 k_B$ K and $A_2 = -0.069 k_B$ K producing $T_N = 5.5$ K for pure $EuTiO_3$ represent the antiferromagnetic coupling between the nearest neighbors and the ferromagnetic coupling between the next-nearest neighbors, respectively. Here h is the external magnetic field parallel to the z axis. $[i,j]$ and $\langle i,j \rangle$ denote the summation over the next-nearest neighbors and the nearest neighbors once, respectively. Two parameters θ_i and C_j are introduced to describe the occupation status of the magnetic ions and the nonmagnetic ones on the lattice site. They are defined as $\theta_i(C_j) = 0$ if $i(j)$ site is occupied by nonmagnetic ions and $\theta_i(C_j) = 1$ if $i(j)$ site is occupied by magnetic ions.

Following Ref. 32, in which the coupling term was put forward as an interaction of electrical polarization and the z component Ising spins, the coupling term between the magnetic and electrical subsystems in the present compound is proposed, within the framework of the TIM and Heisenberg model, as

$$H^{me} = -g \sum_{\langle i,j \rangle} \sum_{k,l} \sigma_k^z \sigma_l^z \vec{S}_i \cdot \vec{S}_j \theta_i C_j, \tag{4}$$

where g is the coupling coefficient.

First, we focus on the electrical subsystem, considering electrical-magnetic coupling and impurity effect. As is shown in our previous work,[36] the random-bond model usually used in the magnetic mixed system is applied to this electrical subsystem. The distribution functions of J, Ω, and μ can be expressed as following:

TABLE I. Fitting parameters of pure $BaTiO_3$ and $EuTiO_3$.

	Ω (J)	μ (e Å)
$BaTiO_3$	4.9×10^{-21}	2.17
$EuTiO_3$	2.2×10^{-21}	0.81

$$P(J) = x\,\delta(J - J_1) + (1-x)\,\delta(J - J_2), \tag{5}$$

$$P(\Omega) = x\,\delta(\Omega - \Omega_1) + (1-x)\,\delta(\Omega - \Omega_2), \tag{6}$$

$$P(\mu) = x\,\delta(\mu - \mu_1) + (1-x)\,\delta(\mu - \mu_2), \tag{7}$$

where x and $1-x$ are the concentration of Ba and Eu ions, respectively, J_1, Ω_1, and μ_1 are the corresponding parameters for pure $BaTiO_3$, and J_2, Ω_2, and μ_2 are those for pure $EuTiO_3$. The fitting parameters of pure $BaTiO_3$ are given in Ref. 37. Within the framework of a mean-field approximation we fit the experimental data and obtain J_2, Ω_2, and μ_2 of pure $EuTiO_3$.[4] We show some of these parameters in Table I. For pure $BaTiO_3$, a very important aspect is that it undergoes the first-order phase transition, which makes it necessary to take into account the modification from the ferroelectric distortion. So the nearest-neighbor pseudospin interaction constant in pure $BaTiO_3$ is assumed to be modified as following:

$$J_1 = J_{10}(1 + F_2 P^2 + F_4 P^4 + F_6 P^6), \tag{8}$$

where P is the polarization, $J_{10} = 2.3 \times 10^{-20}$ J is the original interaction constant when the ferroelectric distortion is not considered. $F_2 = 2.6$ m^4/C^2, $F_4 = 16$ m^8/C^4, and $F_6 = -860$ m^{12}/C^6 describe the contribution of the ferroelectric distortion.[37] According to Eq. (8) we find that the modification on the interaction constant leads to the same results as the addition of the four-body, six-body, and eight-body interactions under the mean-field approximation on single ion, which explains the experimental results more appropriately and accurately.[37,38] Under the mean-field approximation, the single-ion Hamiltonian for the electrical subsystem including the coupling term can be written as

$$H_k^E = -\Omega \sigma_k^x - J(g) \langle\langle \sigma^z \rangle\rangle \sigma_k^z - 2\mu(E + E_0) \sigma_k^z, \tag{9}$$

where

$$J(g) = J + 6 z_1 g \langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle \tag{10}$$

and $z_1 = 4$ is the number of the magnetic spin pairs that directly affects each pair of pseudospins. $\langle\langle\,\rangle\rangle$ represents the total average including both the thermoaverage and the compositional average. It is obvious that the magnetic effect on the electrical subsystem is embodied by its modification on the pseudospin interaction. According to quantum statistical theory the thermoaverage of the pseudospin is

$$\langle\sigma^z\rangle=\frac{\mathrm{Tr}\sigma^z\exp(-\beta H_k^E)}{\mathrm{Tr}\exp(-\beta H_k^E)}$$
$$=\frac{J(g)\langle\langle\sigma^z\rangle\rangle+2\mu(E+E_0)}{\sqrt{\Omega^2+[J(g)\langle\langle\sigma^z\rangle\rangle+2\mu(E+E_0)]^2}}\times\tanh\left(\frac{\sqrt{\Omega^2+[J(g)\langle\langle\sigma^z\rangle\rangle+2\mu(E+E_0)]^2}}{2k_BT}\right),\tag{11}$$

where k_B is the Boltzmann constant. The thermoaverage polarization and the total mean polarization are $\langle P\rangle=2N\mu\langle\sigma^z\rangle$ and $\langle\langle P\rangle\rangle=2N\mu\langle\langle\sigma^z\rangle\rangle$, where N is the density of dipolar moment. Thus from Eq. (11) we easily get

$$\langle P\rangle=\frac{N\mu[J(g)\langle\langle P\rangle\rangle+4N\mu^2(E_0+E)]}{\sqrt{4N^2\mu^2\Omega^2+[J(g)\langle\langle P\rangle\rangle+4N\mu^2(E_0+E)]^2}}\times\tanh\frac{\sqrt{4N^2\mu^2\Omega^2+[J(g)\langle\langle P\rangle\rangle+4N\mu^2(E_0+E)]^2}}{4N\mu k_BT}.\tag{12}$$

Actually the density of dipolar moment in $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ decreases with Ba doping because of its larger ion. This feature can be described by a linear Vegard law:[39] $\Delta a=0.1x$ Å, where Δa is the increment of EuTiO_3 lattice constant in a sample with Ba concentration x and the lattice parameter a_0 in pure EuTiO_3 is ≈ 3.905 Å. As far as the compositional average is concerned, we get

$$\langle\langle P\rangle\rangle=\int_{J,\Omega,\mu}\langle P\rangle P(J)P(\Omega)P(\mu)dJd\Omega d\mu,\tag{13}$$

$$N=\frac{1}{(a_0+\Delta a)^3}.\tag{14}$$

The dielectric susceptibility is

$$\chi(g)=\frac{1}{\varepsilon_0}\frac{\partial\langle\langle P\rangle\rangle}{\partial E}\bigg|_{E=0},\tag{15}$$

and the dielectric constant is

$$\varepsilon(g)=A+\chi(g).\tag{16}$$

Here A is the background dielectric constant and assumed to change with the impurity content.

Through theoretical calculation the dielectric susceptibility including the coupling effect for pure EuTiO_3 is obtained as

$$\chi(g)=\frac{1}{\varepsilon_0}\frac{\partial\langle\langle P\rangle\rangle}{\partial E}\bigg|_{E=0}=\chi(0)(1+\beta\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle+\beta^2\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle^2+\cdots),\tag{17}$$

where

$$\chi(0)=\frac{N\mu_2^2/\varepsilon_0}{\Omega_2\coth(\Omega_2/2k_BT)/2-J_2/4}\tag{18}$$

is the dielectric constant without including the coupling effect and

$$\beta=\frac{6\chi(0)g\varepsilon_0}{N\mu_2^2}.\tag{19}$$

Although the mean-field approximation is employed here, the expression of $\chi(0)$ for pure EuTiO_3 is in good agreement with Barret formula,[40] which well describes the quantum effects in quantum paraelectrics. In fact the quadratic term in $\chi(g)$ can be omitted because of the intrinsic properties of EuTiO_3. Thus the dielectric constant for pure EuTiO_3 can be obtained as

$$\varepsilon(g)=\varepsilon(0)(1+\alpha\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle),\tag{20}$$

where

$$\alpha=\frac{\chi(0)}{A+\chi(0)}\beta\tag{21}$$

and $\varepsilon(0)=A+\chi(0)$ is the dielectric constant excluding the coupling interaction. From above we conclude that α is determined by several intrinsic physical quantities. Our results above are in good agreement with the experimental data for pure EuTiO_3, which proves the rationality of our proposed model.

As far as the impurity-doped cases are concerned, Eqs. (20) and (21) are still applicable. But for the impurity-doped cases, $\varepsilon(0)$ is a more complicated expression and related to x, E_0, A, N, and the distribution function of J, Ω, and μ, which at the same time leads to the intrinsic decrease of α. Through our theoretical calculation, we fit the numerical data of the intrinsic field-induced polarization and get its analytical relation to $\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle$:

$$\langle\langle P\rangle\rangle(g)=\langle\langle P\rangle\rangle(0)(1+\beta\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle).\tag{22}$$

To investigate how the dielectric constant varies under different conditions of spin correlation, we take into account the spin correlation in the coupling system. Then the Hamiltonian for the magnetic subsystem can be written as

$$H^M=H^m+H^{me}=\sum_{\langle i,j\rangle}A_1(g)\vec{S}_i\cdot\vec{S}_j\theta_iC_j+A_2\sum_{[i,j]}\vec{S}_i\cdot\vec{S}_j\theta_iC_j-\sum_i\vec{h}\cdot\vec{S}_i\theta_i,\tag{23}$$

where

$$A_1(g)=A_1-z_2g\langle\langle\sigma_k^z\sigma_l^z\rangle\rangle\tag{24}$$

and $z_2=4$ is the number of the pseudospin pairs that directly affect each pair of spin correlation. One can see that the electrical effect on the magnetic system is realized by the modification on the antiferromagnetic interaction. This magnetic subsystem can be divided into two sublattices a and b. Thus

$$H^M = H_a + H_b, \tag{25}$$

where H_a and H_b are the Hamiltonians belonging to a and b sublattices, respectively. Under the mean-field approximation,

$$H_a = H_a^x \sum_{ai} S_{ai}^x \theta_a + H_a^z \sum_{ai} S_{ai}^z \theta_a \tag{26}$$

and

$$H_b = H_b^x \sum_{bi} S_{bi}^x C_b + H_b^z \sum_{bi} S_{bi}^z C_b, \tag{27}$$

where

$$H_{a(b)}^x = 6A_1(g)\langle\langle S_{b(a)}^x \rangle\rangle + 12A_2 \langle\langle S_{a(b)}^x \rangle\rangle, \tag{28}$$

$$H_{a(b)}^z = -h + 6A_1(g)\langle\langle S_{b(a)}^z \rangle\rangle + 12A_2 \langle\langle S_{a(b)}^z \rangle\rangle. \tag{29}$$

Here x, z denote the spin components. Thus the thermoaverage of spin components of different sublattices can be obtained as

$$\langle S_a^z \rangle = \frac{-H_a^z}{2\sqrt{(H_a^x)^2 + (H_a^z)^2}} \times \frac{\sum_{i=1}^{4} (2i-1)\sinh\left(\frac{(2i-1)\theta_a}{2k_B T}\sqrt{(H_a^x)^2 + (H_a^z)^2}\right)}{\sum_{i=1}^{4} \cosh\left(\frac{(2i-1)\theta_a}{2k_B T}\sqrt{(H_a^x)^2 + (H_a^z)^2}\right)}, \tag{30}$$

$$\langle S_b^z \rangle = \frac{-H_b^z}{2\sqrt{(H_b^x)^2 + (H_b^z)^2}} \times \frac{\sum_{i=1}^{4} (2i-1)\sinh\left(\frac{(2i-1)C_b}{2k_B T}\sqrt{(H_b^x)^2 + (H_b^z)^2}\right)}{\sum_{i=1}^{4} \cosh\left(\frac{(2i-1)C_b}{2k_B T}\sqrt{(H_b^x)^2 + (H_b^z)^2}\right)}, \tag{31}$$

$$\langle S_a^x \rangle = \frac{H_a^x}{H_a^z}\langle S_a^z \rangle, \tag{32}$$

$$\langle S_b^x \rangle = \frac{H_b^x}{H_b^z}\langle S_b^z \rangle. \tag{33}$$

We consider the distribution function of θ_a and C_b:

$$P(\theta_a) = \frac{1-x}{2}\,\delta(\theta_a - 1) + \frac{x}{2}\,\delta(\theta_a), \tag{34}$$

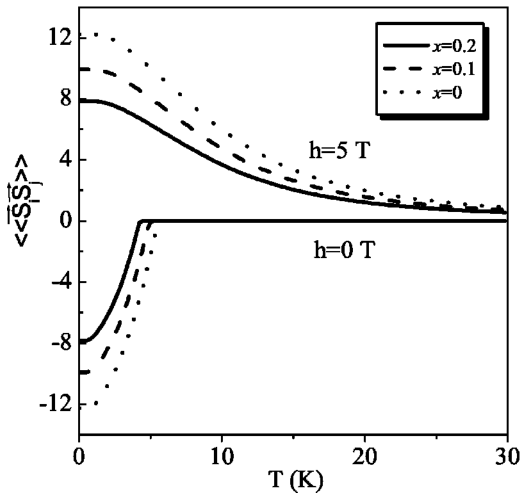

FIG. 1. Temperature dependence of spin correlation $\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle$ between the nearest neighbors for different impurity contents.

$$P(C_b) = \frac{1-x}{2}\,\delta(C_b - 1) + \frac{x}{2}\,\delta(C_b). \tag{35}$$

The total average including the compositional average for magnetization can be obtained as

$$\langle\langle S_{a(b)}^{z(x)} \rangle\rangle = \frac{\int_{\theta_a, C_b} \langle S_{a(b)}^{z(x)} \rangle P(\theta_a) P(C_b)\, d\theta_a dC_b}{\int_{\theta_a, C_b} P(\theta_a) P(C_b)\, d\theta_a dC_b}. \tag{36}$$

The spin correlation between the nearest neighbors can be approximately decoupled as

$$\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle = \langle\langle S_a^x \rangle\rangle \langle\langle S_b^x \rangle\rangle + \langle\langle S_a^z \rangle\rangle \langle\langle S_b^z \rangle\rangle. \tag{37}$$

For this complicated $Eu_{1-x}Ba_xTiO_3$ system, where coupling exists between the magnetic and electrical subsystems, one should consider the subsystem results obtained by including the coupling term $-g\Sigma_{\langle i,j\rangle}\Sigma_{k,l}\sigma_k^z \sigma_l^z \vec{S}_i \cdot \vec{S}_j \theta_i C_j$.

III. RESULTS AND DISCUSSION

We obtain the main features of $Eu_{1-x}Ba_xTiO_3$ $(0 \leqslant x \leqslant 0.2)$ by adjusting A and E_0. For $x = 0$, 0.1, and 0.2, A is 181, 230, and 530, and E_0 is 0 kV/mm, 1.9 kV/mm, and 2.1 kV/mm, respectively. By solving Eqs. (20), (21), (36), and (37), we fit the experimental dielectric constant in the absence of the magnetic field. We obtain the coupling coefficient g as $0.09k_B$ K, $0.11k_B$ K, and $0.21k_B$ K for $x = 0$, 0.1, and 0.2, respectively. We use these parameters to study the coupling effect on the magnetic and electrical subsystems.

The spin correlation $\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle$ versus temperature under different magnetic fields and at different impurity content is shown in Fig. 1. The variation of spin configuration can be realized by varying the temperature and external magnetic field at the same impurity content. Meanwhile T_N decreases with the increase of the impurity content. Although there still exists some deviations from the experimental results, e.g., T_N

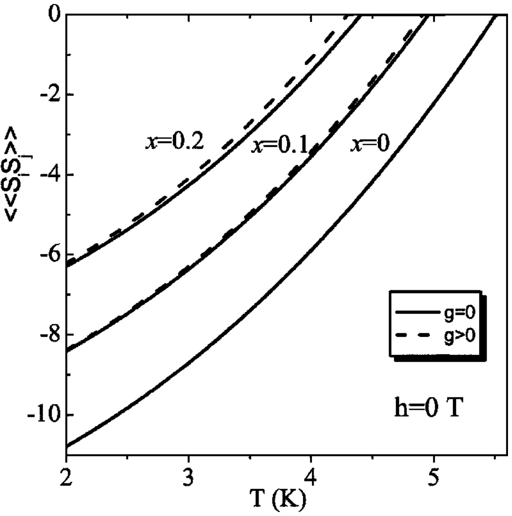

FIG. 2. Comparison of different coupling effects on the temperature dependence of spin correlation $\langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle$ for different impurity contents.

is a little higher than experimental data because of the model simplicity and approximation, the main feature is satisfactorily exhibited. It is easy to find the trend similarity between the spin correlation and the dielectric constant in $Eu_{1-x}Ba_xTiO_3$ $(0 \leqslant x \leqslant 0.2)$.

In fact, there is another important factor that affects the spin configuration in this system. In Fig. 2, we compare the coupling effect on the magnetic subsystem of $Eu_{1-x}Ba_xTiO_3$ for different impurity contents ($h = 0$ T). T_N shows additional evident decrease when the coupling interaction is taken into account ($g > 0$) and this coupling interaction has greater effect on the spin correlation for higher impurity content. For the case $x = 0$, however, the coupling interaction has no effect on the magnetic subsystem. These can be explained from the variation of Hamiltonian. Because of the polarization in the electrical subsystem, the antiferromagnetic coupling constant A_1 diminishes to $A_1 - z_2 g \langle\langle \sigma_k^z \sigma_l^z \rangle\rangle$, which favors the decrease of T_N; and owing to the increase of intrinsic field-induced polarization with the increase of the impurity content, T_N has a more evident decrease for higher impurity content.

The temperature dependence of the dielectric constant for different impurity content under different magnetic fields is shown in Fig. 3. Similar experimental results have been reported in Ref. 4 [Fig. 4(a)] for $Eu_{1-x}Ba_xTiO_3$. The dielectric constant increases with the impurity content within the whole temperature range because for the case $0 < x < x_c$, the quantum paraelectric state becomes fragile with the increase of impurity content and the deviation from the Curie-Weiss law is reduced, while at the same time the ferroelectric phase transition does not occur. At low temperatures, the dielectric constant and the spin correlation exhibit similar features (see Fig. 1), indicating coupling between the electrical and magnetic subsystems. We believe that the anomalies are caused by the coupling interaction because below $T_N(h = 0$ T) the pseudospin interaction constant is decreased due to the antiferromagnetic ordering, which favors the reduction of the dielectric constant. If the temperature is higher than T_N, the spin correlation is zero and it has no effect on the dielectric constant. When the magnetic field $h = 5$ T is applied and the ferromagnetic ordering appears, however, the pseudospin interaction constant increases, favoring the increase of the dielectric constant.

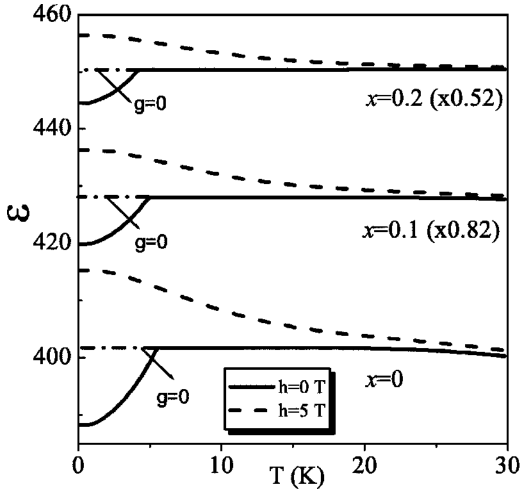

FIG. 3. Dielectric constants of $Eu_{1-x}Ba_xTiO_3$ with $x = 0$, 0.1, and 0.2 as a function of temperature under different magnetic fields. The data have been multiplied by 0.82 for $x = 0.1$ and 0.52 for $x = 0.2$ for clarity.

The temperature dependence of the intrinsic field-induced mean polarization for different impurity content and under different magnetic fields also shows its interesting features, as is shown in Fig. 4. Magnetic-electrical coupling interaction significantly contributes to the mean polarization, which is also attributed to the modification of the pseudospin interaction constant by the spin configuration. That is, the antiferromagnetic ordering favors the decrease of the polarization while ferromagnetic ordering does the opposite. From our numerical calculation, we fitted the theoretical data of polarization and obtain the analytical formula as $\langle\langle P \rangle\rangle(g) = \langle\langle P \rangle\rangle(0)(1 + \beta \langle\langle \vec{S}_i \cdot \vec{S}_j \rangle\rangle)$, from which the relation be-

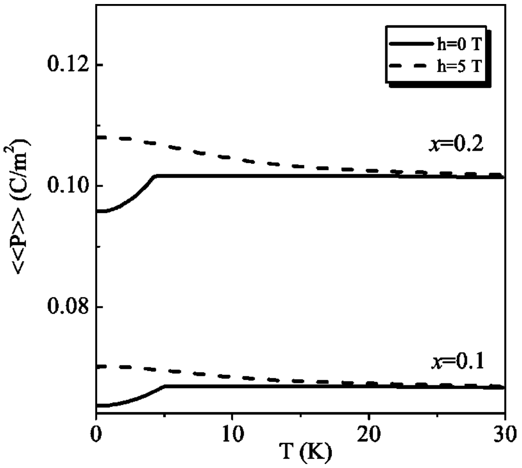

FIG. 4. Temperature dependence of the intrinsic field-induced polarization for different impurity contents under different magnetic fields.

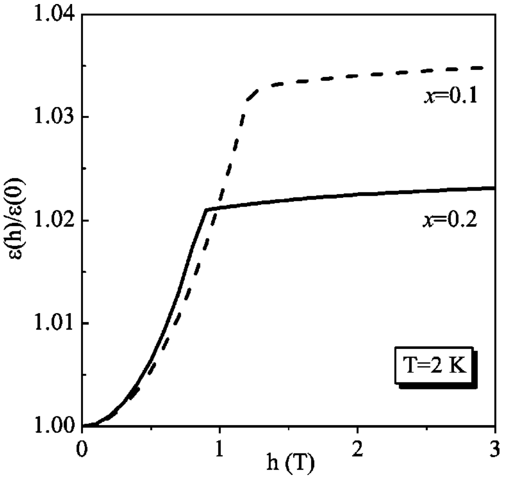

FIG. 5. Magnetic-field dependence of the dielectric constant (normalized to the values under zero field) at 2 K for different impurity contents.

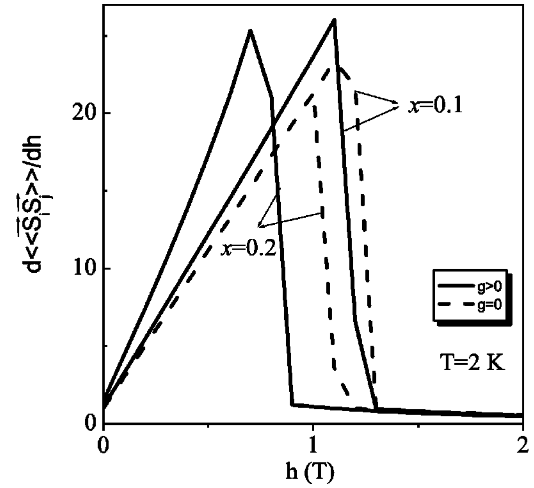

FIG. 6. Magnetic-field dependence of the spin-correlation variation for different impurity contents at 2 K.

tween the dielectric constant and the spin correlation seems more comprehensible.

Magnetic-field dependence of the dielectric constant (normalized to the values at zero field) at 2 K for $Eu_{1-x}Ba_xTiO_3$ for $x=0.1$ and $x=0.2$ is shown in Fig. 5. The change of the dielectric constant with magnetic field looks reduced with Ba doping. This is partly because the magnetic $EuTiO_3$ is diluted by nonmagnetic Ba ions, which can be seen from the formula:

$$\frac{\varepsilon(h)}{\varepsilon(0)}=\frac{1+\alpha\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle(h)}{1+\alpha\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle(0)}.$$

Taking account of the dilution effect, $\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle$ for $x=0$ should be replaced by $(1-x)^2\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle$. At the same time α is intrinsically reduced via Eq. (21). Furthermore, it should be noted that the initial slope of the dielectric constant against magnetic field rather increases with Ba doping in spite of the decrease of α because of the faster increase of magnetization with magnetic field for higher impurity content, as can be seen in Fig. 6. We obtain the formula:

$$\frac{\partial}{\partial h}\left(\frac{\varepsilon(h)}{\varepsilon(0)}\right)\propto\frac{\partial}{\partial h}(\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle_{(h)}),$$

from which we believe that the initial larger slope of the dielectric constant for $x=0.2$ is mainly determined by the initial faster increase of $\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle$ versus h. A more profound reason for this dielectric feature originates from the coupling effect on the magnetic subsystem. If we omit this effect, the initial larger slope of the dielectric constant nearly disappears (see Fig. 6, dashed line). A good agreement between our theoretical results (Fig. 5) and experimental data [Fig. 4(b) in Ref. 4] has been observed for $Eu_{1-x}Ba_xTiO_3$, demonstrating the reliability of our present models.

Figure 7 shows the magnetic-field dependence of the intrinsic field-induced electrical polarization for $x=0.1$ and $x=0.2$. The anomalies are caused by coupling between magnetic and electrical subsystems; and the initial larger slope for $x=0.2$ is also attributed to the initial faster increase of $\langle\langle\vec{S}_i\cdot\vec{S}_j\rangle\rangle$ versus h.

IV. CONCLUSIONS

Pure $EuTiO_3$ is regarded as both a typical type-*G* antiferromagnet with $S=7/2$ and a quantum paraelectric with a perovskite crystal structure. This special property makes the dielectric constant for pure $EuTiO_3$ as well as for its impurity-doped system deviate from the behavior in normal quantum paraelectric. Such an interesting phenomenon has been observed in experiments and indicates the existence of coupling between the magnetism and dielectric properties in them. In the present work we propose an appropriate coupling term to describe interaction between the magnetic and electric subsystem in $Eu_{1-x}Ba_xTiO_3$. Within the framework of random-bond transverse-field Ising model for electrical subsystem and site-dilution Heisenberg model for magnetic subsystem, we investigate the coupling between the magnetism and di-

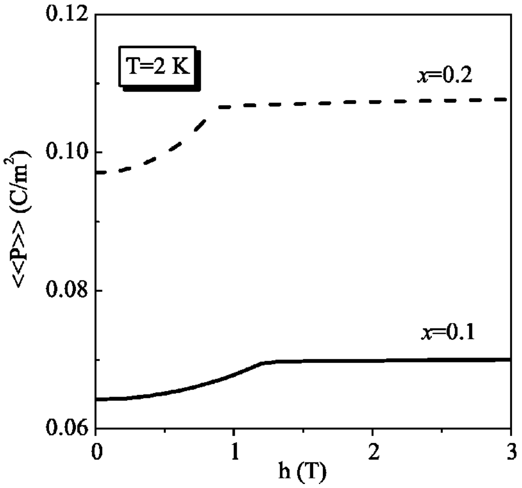

FIG. 7. Magnetic-field dependence of the intrinsic field-induced polarization for different impurity contents at 2 K.

electric properties. Theoretically, we obtain the analytic relation between dielectric constant and spin correlation, which is in good agreement with the experimental results for $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$. Our numerical calculation shows that many aspects of the magnetism and dielectric properties observed in $\mathrm{Eu}_{1-x}\mathrm{Ba}_x\mathrm{TiO}_3$ can be described by our theoretical framework involving coupling interaction between magnetic and electrical subsystem. In addition, we find that impurity doping affects not only the strength of coupling (g) between electrical and magnetic subsystem, but also polarization and spin correlation. Furthermore, impurity doping also causes the intrinsic frozen field, which increases with increasing doping concentration. By fitting with experimental data, we discuss the effect of doping and external magnetic field on the dielectric properties. The effect of coupling and doping on their magnetic properties have also been discussed, especially for higher impurity content.

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