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A possible coupling mechanism between magnetism and dielectric properties in $EuTiO_3$

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The dielectric constant of an incipient ferroelectric $EuTiO_3$ exhibits a sharp decrease at about 5.5K, at which the antiferromagnetic ordering of the Eu spins simultaneously appears. This fact indicates the existence of a coupling between the magnetism and dielectric properties of $EuTiO_3$. We propose a possible coupling mechanism between the magnetic and electrical subsystems as $-g\sum_{l}\sum_{\langle i,j\rangle} q_l^2 \vec{S}_i \cdot \vec{S}_j$. In the framework of soft-mode theory, we have obtained analytically a dielectric constant expression related to the spin correlation of nearest neighbours of Eu ions.

Keywords: coupling mechanism, magnetism, dielectric property, soft-mode theory
PACC: 7550E, 7700

1. Introduction

The coupling between magnetism and transport properties in metals can produce various interesting phenomena, such as colossal magnetoresistance in perovskite manganites.[1−3] The Hund rule dominates in this class of compounds, where the localized spins in the t_{2g} state strongly couple with the itinerant electrons in the e_g state. If a magnetic field is applied under such a condition, the configuration of the localized spins varies, giving rise to a large magnetoresistance. At the same time, it is definite that the coupling between magnetism and dielectric properties may exist in certain magnetic insulators where the configuration of the localized spins affects, to some extent, their dielectric properties. $EuTiO_3$ is a good example in this case. Susceptibility measurements show that $EuTiO_3$ is one of the few antiferromagnets with a positive Curie–Weiss temperature.[4] And its Néel temperature is about T_N=5.5K.[5] The crystal structure of $EuTiO_3$ is presented in Fig.1. It exhibits a typical structure of perovskite titanates, where Eu ions are responsible for the antiferromagnetic ordering and its spin vector lies in the ab plane while the ion motion of the soft-phonon mode (here mainly Ti ion) with a $T_{1\mu}$ symmetry is along the c-axis.

It has been reported[5] that the dielectric constant of $EuTiO_3$ exhibits a sharp decrease at 5.5K, which is its Néel temperature T_N. As is known, $EuTiO_3$ is an incipient ferroelectric, its dielectric constant saturates at a low temperature. This gives a clue that a possible relation exists between the magnetic and electrical subsystems. Given that the soft-phonon mode with a low frequency is responsible for the dielectric properties via the soft-mode theory $\chi_{\vec{q}} = \dfrac{1}{m(\omega_{\vec{q}}^2 - \omega^2)}$ in $EuTiO_3$, a plausible speculation is that the variation of the spin configuration at the Eu site near and below T_N will affect the behaviour of the soft-phonon mode and lead to special dielectric properties. But there is still a challenging question: what is the possible coupling mechanism between magnetism and dielectric properties?

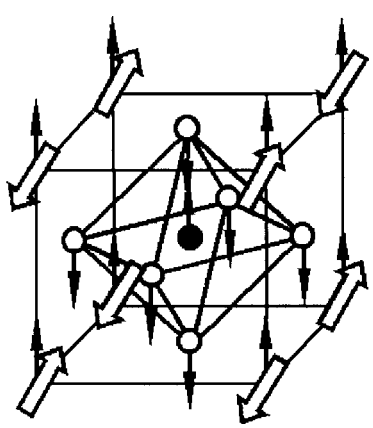


Fig.1. The crystal structure of $EuTiO_3$. Empty and solid circles represent O and Ti atoms, respectively. The white thick arrows are the antiferromagnetic ordering of Eu spins. The black thin arrows exhibit the atomic motion of the soft-phonon mode.

Many years ago, it was proposed[6] that the dielectric constant in some ferroelectric crystals with magnetic long-range order coexisting, so-called ferroelectromagnetic, should have an anomaly at the magnetic ordering temperature. The argument was based on the following considerations. Generally, a term of the type $\xi p^2 l^2$ is allowed in a free-energy expression irrespective of the symmetry, where l is a vector parameter representing the long-range magnetic ordering. The non-zero value of l affects the polarization p through this term. In the $EuTiO_3$ case, magnetic ions are in an s-type orbital and the exchange interaction is isotropic. The Heisenberg model is suitable for describing this magnetic system. On the other hand, the experimental data[5] available evidently propose the relation between the dielectric constant and spin correlation $\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle$ as $\varepsilon = \varepsilon_0(1 + \alpha \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle)$. In the present work, we first include the coupling term of electric and magnetic subsystems in the Hamiltonian for $EuTiO_3$. Then the Hamiltonian is solved with the mean-field and soft-mode theory, to obtain the dielectric constant.

2.Models and analysis

We consider the Hamiltonian for a three-dimensional cubic system with periodic boundary conditions. Two parameters, q_l and S_i, are used here to represent the electrical displacement at the Ti site, which mainly causes the soft-mode of $T_{1\mu}$, and the Heisenberg spin at the Eu site, respectively. In addition, the coupling interaction between the electrical and magnetic subsystems is taken into account. The Hamiltonian for this system can be written as

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

where H^e denotes the Hamiltonian for the electrical subsystem, H^m is the Hamiltonian for the magnetic subsystem and H^{me} is the coupling interaction between the two subsystems. Here, the soft-mode theory in the mean-field approximation is applied to solve H^e. According to the soft-mode theory, the atoms vibrate like a harmonic oscillator with a small additional anharmonic part, i.e. q_l at each site is subjected to a single-well potential. Thus H^e in the absence of an electric field can be written as[7,8]

$$H^e = \sum_l \left[\frac{p_l^2}{2m} + V(q_l) \right] - \frac{1}{2} \sum_l \sum_{l'} \nu_{ll'} q_l q_{l'}, \tag{2}$$

where p_l is the momentum at site l, $V(q_l)$ is the localized potential function, and $\frac{1}{2} \sum_l \sum_{l'} \nu_{ll'} q_l q_{l'}$ denotes the two-body interaction potential. We use the simplest form to describe the anharmonic motion at Ti site. Thus

$$V(q_l) = \frac{1}{2} m \Omega_0^2 q_l^2 + \frac{1}{4} \gamma q_l^4, \tag{3}$$

where Ω_0 is the inherent frequency, $\frac{1}{2} m \Omega_0^2 q_l^2$ is the harmonic part and $\frac{1}{4} \gamma q_l^4$ is the anharmonic part.

The interaction between Eu $4f$ spins originates from (i) the superexchange(antiferromagnetic) through the O $2p$ state, and also from (ii) the indirect exchange through the Eu $5d$ state. So H^m with $S = \frac{7}{2}$ can be written as

$$H^m = \sum_{\langle i,j \rangle} J_1 \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{[i,j]} J_2 \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \sum_i \boldsymbol{h} \cdot \boldsymbol{S}_i, \tag{4}$$

where S_i is the Heisenberg spin at the Eu site i, and the exchange integrals J_1 and J_2 represent the antiferromagnetic coupling between the nearest neighbours and the ferromagnetic coupling between the next-nearest neighbours, respectively. Here h is the external magnetic field parallel to the z-axis. $[i,j]$ and $\langle i,j \rangle$ denote the once summation over the next-nearest neighbours and the nearest neighbours, respectively.

Now, we consider the magnetic–lattice interaction H^{me}. For $EuTiO_3$, the wavefunction of the anion plays an important role in superexchange coupling between nearest-neighbour Eu spins, because the exchange integral may be mediated via the p election of the anion, i.e. $J_1 = J_1(r_O - r_{Eu})$. Moreover, the oxygen ion is related to the motion of the soft-phonon mode with $T_{1\mu}$ symmetry. If this ion is displaced from its equilibrium position r_O by a distance u_O, the variation of superexchange interaction energy between nearest-neighbour Eu ions through the O $2p$ state is given by

$$\begin{aligned} &\sum_{\langle i,j \rangle} \{ J_1(r_O + u_O - r_{Eu}) - J_1(r_O - r_{Eu}) \} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \\ &\approx \sum_{\langle i,j \rangle} \left\{ u_O \nabla J_1(r_O - r_{Eu}) \right. \\ &\quad \left. + \frac{1}{2!} u_O^2 \nabla^2 J_1(r_O - r_{Eu}) \right\} \boldsymbol{S}_i \cdot \boldsymbol{S}_j. \end{aligned} \tag{5}$$

Because the relative displacement u_O of the oxygen ion is related to the motion of the Ti ion, we make an approximation that u_O is proportional to the displacement q of Ti ion, thus the final expression of H^{me} is given by

$$H^{me} = -g \sum_l \sum_{\langle i,j \rangle} q_l^2 \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \tag{6}$$

where g is the coupling coefficient to scale the coupling strength. Here only the quadratic term of q_l is taken because of the time reversal and space reversal symmetries. Now we deal with the electrical subsystem, taking into consideration the magnetic effect. Then under the mean-field approximation, the single-ion Hamiltonian can be written as

$$\begin{aligned} H_l^E =& H_l^e + H_l^{me} \\ =& \frac{p_l^2}{2m} + \left(\frac{1}{2}m\Omega_0^2 - z_1 g\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle\right) q_l^2 \\ &+ \frac{1}{4}\gamma q_l^4 - \sum_{l'} \nu_{ll'}\langle q_{l'}\rangle q_l, \end{aligned} \tag{7}$$

where z_1 is the number of the spin correlations that will directly affect the motion of Ti in one unit cell and $\frac{1}{4}\gamma q_l^4$ can be regarded as the small perturbation part. For convenience, in further discussion we assume $b = \frac{2z_1 g}{m\Omega_0^2}\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle$ and $\Omega_0(g) = \Omega_0\sqrt{1-b}$. Here the magnetic effect on the electrical subsystem is embodied by $\Omega_0(g)$. Thus we have

$$H_l^E = \frac{p_l^2}{2m} + \frac{1}{2}m\Omega_0^2(g)q_l^2 + \frac{1}{4}\gamma q 4_l - \sum_{l'} \nu_{ll'}\langle q_{l'}\rangle q_l. \tag{8}$$

The frequency of the soft-phonon mode is given according to the soft-mode theory,

$$m\omega_{\vec{q}}^2(g) = m\Omega_0^2(g) + 3\gamma\sigma_T - \nu_{\vec{q}}, \tag{9}$$

where

$$\nu_{\vec{q}} = \sum_{l'} \nu_{ll'} \exp[-\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{R}_l - \boldsymbol{R}_{l'})] \tag{10}$$

is the interaction potential for the wave vector $\boldsymbol{q}$. Up to now, the key point is how to calculate the fluctuation of displacement $\sigma_T = \langle q_l - \langle q_l\rangle^2\rangle$. Since $EuTiO_3$ is an incipient ferroelectrics, the quantum effect is very important at very low temperatures, so the quantum statistics must be adopted. At the same time, we notice that no ferroelectric phase transition takes place in the incipient ferroelectrics, and the average displacement is zero. Thus, the fluctuation of displacement at temperature T can easily be obtained using quantum statistics and perturbation theory:

$$\begin{aligned} \sigma_T =& \langle q_l - \langle q_l\rangle^2\rangle \\ =& \frac{\hbar}{2m\Omega_0(g)}\mathrm{Coth}\left(\frac{\hbar\Omega_0(g)}{2k_BT}\right) \\ &- \frac{3\gamma}{16m^3\Omega_0^4(g)}\left[\mathrm{Coth}^2\left(\frac{\hbar\Omega_0(g)}{2k_BT}\right) + 1\right]. \end{aligned} \tag{11}$$

For $EuTiO_3$ the soft-phonon mode is in the centre of the Brillouin zone ($\boldsymbol{q}$=0). Therefore according to the single mode theory under the mean-field approximation, the frequency of the soft-phonon mode can be obtained by

$$\begin{aligned} m\omega^2(g) =& m\Omega_0^2(g) + 3\gamma\sigma_T - \nu_0 \\ =& \frac{3\gamma}{m\Omega_0^2(g)}\left[\frac{\hbar\Omega_0(g)}{2}\mathrm{Coth}\left(\frac{\hbar\Omega_0(g)}{2k_BT}\right) - k_BT_0\right], \end{aligned} \tag{12}$$

where

$$k_BT_0 = \frac{m\Omega_0^2(g)}{3\gamma}\Big[\nu_0 - m\Omega_0^2(g)\Big]. \tag{13}$$

Obviously, if the coupling effect is not included, i.e. g=0, Eq.(12) is just the expression of the frequency of the soft-phonon mode for normal incipient ferroelectrics. The frequency of the soft-phonon mode does not freeze even close to 0K. In order to directly show how the spin correlation has an effect on the behaviour of the soft-phonon mode, we arrange Eq.(12) as follows

$$m\omega^2(g) \approx m\omega^2(0)(1 - \beta\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle), \tag{14}$$

where

$$\begin{aligned} \beta =& \frac{2z_1 g}{m^2\Omega_0^2\omega^2(0)}\left[m\Omega_0^2 - \frac{3\gamma\hbar}{4m\Omega_0}\mathrm{Coth}\Big(\frac{\hbar\Omega_0(g)}{2k_BT}\Big)\right. \\ &\left. + \frac{\hbar\Omega_0}{2k_BT\sinh^2\Big(\frac{\hbar\Omega_0(g)}{2k_BT}\Big)}\right]. \end{aligned} \tag{15}$$

Here $\omega(0)$ is the frequency of the soft-phonon mode, as the coupling interaction is not considered, and it is temperature-independent at very low temperatures. Because the coupling interaction only exists near the Néel ordering temperature, β can be approximately written as

$$\beta = \frac{2z_1 g}{m^2\Omega_0^2\omega^2(0)}\left[m\Omega_0^2 - \frac{3\gamma\hbar}{4m\Omega_0}\right]. \tag{16}$$

Naturally, the static susceptibility, which embodies the dielectric constant, is found

$$\chi \approx \frac{1}{m\omega^2(0)}(1 + \beta\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle) = \chi(0)(1 + \beta\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle), \tag{17}$$

where $\chi(0)$ is the static susceptibility when the coupling interaction is not included. Thus the dielectric constant can be derived from the above expressions

$$\varepsilon = \varepsilon(0)(1 + \alpha\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle), \tag{18}$$

where

$$\varepsilon(0) = A + \chi(0) \tag{19}$$

and

$$\alpha = \frac{\chi(0)\beta}{A + \chi(0)}. \tag{20}$$

Here A is the background dielectric constant. Equation (18) is in good agreement with the dielectric property fitted from the experimental data.[5] Undoubtedly, near T_N, the appearance of an antiferromagnetic spin correlation leads to a sharp decrease in dielectric constant. Furthermore, if fitting the experimental data in the absence of a magnetic field,[5] we obtain the coupling coefficient g to be 9.42×10^{-7}, which is small but plays an important role in the behaviour of the dielectric properties.

3. Summary

$EuTiO_3$ is regarded as a typical Néel antiferromagnet with $S = \frac{7}{2}$ at the Eu^{2+} site, as well as an incipient ferroelectric with a perovskite crystal structure. This special property makes its dielectric constant deviate from the behaviour in normal incipient ferroelectrics below the Néel temperature. We have proposed a possible coupling mechanism between its magnetism and dielectric properties as $-g\sum_l \sum_{\langle i,j\rangle} q_l^2 \boldsymbol{S}_i \cdot \boldsymbol{S}_j$ and we obtain analytically the value of the dielectric constant, which is in good agreement with the fitted formula from experimental data.

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