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The study of the coupling mechanism between antiferromagnetic and ferroelectric ordering and thermodynamic properties in ferroelectromagnets

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Abstract

We study the coupling mechanism between antiferromagnetic and ferroelectric ordering that coexist spontaneously at low temperatures. According to the results of experiment and previous theoretical considerations, we propose a possible coupling form related to a combination of electric polar and spin correlation and use it to calculate the thermodynamic properties of a ferroelectromagnetic system, including its magnetization m, polarization p, magnetization susceptibility χ_m, magnetoelectric susceptibility χ_{me} and polarization susceptibility χ_p, in the case of magnetization m perpendicular to polarization p. It is found that the relationship between m, χ_m and χ_{me} is in agreement with that of phenomenological theory, and polarization induced by magnetic coupling leads to an anomaly of χ_p at low temperature, which is consistent qualitatively with experimental results.

1. Introduction

The magnetoelectric (ME) effect has been the subject of intensive theoretical and experimental studies in recent years for its connection with the dielectric and magnetic anomalies that have been observed experimentally in some ferroelectromagnets and quantum paraelectrics [1–4]. An important but debated issue is the nature of the ME coupling mechanism and the form of the interaction.

Spin-ordered material may exhibit an induced magnetization, which is proportional to an applied electric field, and an induced electric moment, which is proportional to an applied magnetic field. These effects are called the electrically induced ME effect $(\mathrm{ME})_E$ and the magnetically induced ME effect $(\mathrm{ME})_H$, respectively. For these kinds of ME effect, it has

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been pointed out by Landau and Lifshitz [5], on the basis of thermodynamic and symmetry considerations, that there exists an allowed term, $\alpha_{i,j}E_iH_j$, in the system free energy, where E and H represent external magnetic and electric fields. According to information on spin configurations provided by ME experiments, on the other hand, based on the molecular-field approximation, de Alcantara and Gehring [6] concluded that an electric field may cause a change in the value of the symmetric exchange $J\vec{s}_i \cdot \vec{s}_j$ and possible forms for this are

$$\frac{1}{2}\sum_{i,j}\alpha E^{u,v}(\varepsilon_i+\varepsilon_j)(s_i^u s_j^v + s_i^v s_j^u)$$

where α is a coupling coefficient, $\varepsilon_i = \pm 1$ on the different sublattices, and u, $v = x$, y, z, respectively. Commonly, these kinds of crystals showing a linear ME effect are called MEs.

A ferroelectromagnetic, however, differs from the MEs in that it shows spontaneous ME effects in addition to the $(\mathrm{ME})_{E,H}$ effects induced by external fields. They are caused by the coexistence in the crystal of spontaneous ferroelectric and magnetic moments. The existence of these gives rise to certain differences in the ME interactions in ferroelectromagnetics as compared with MEs, that is, if a spontaneous polarization arises in a magnetic crystal, then the spin subsystem will be strongly acted on by the internal electric field. The ME energy corresponding to such field values can be of the order of the exchange energy. Accordingly, the interaction energy of ME coupling must be involved in the ferroelectromagnet system Hamiltonian. Experimental evidence also shows that the ME energy in a ferroelectromagnet can be comparable with the magnitudes of the inherent spin and ferroelectric energies [7, 8]. But the form of ME energy and ME coupling mechanism is still an important issue for debate. Janssen [9] and Gao *et al* [10, 11] investigated the phase transitions in a one- and two-dimensional ferroelectromagnetic lattice. They thought the coupling interaction between the electric and magnetic subsystems should be considered as $-\varepsilon_{i,j}gu_k^2 s_i s_j$, where i, j denote the nearest neighbours of site k, but i and j are different sites.

These theories are concerned mainly with the coupling between Ising spin moment and ferroelectric polarization. As a result, they lack a comprehensive understanding of general ME coupling. While in a real crystal, for example $YMnO_3$ and $EuTiO_3$, magnetic orders occur in the basal plane (a, b) and ferroelectric orders arise mainly from displacement of Mn ions or Ti ions along the c axes, we cannot describe the ME coupling simply by the Ising model as long as the anisotropic energy is not too strong. According to [2] and [3], in which thermodynamic properties were investigated experimentally in the hexagonal ferroelectromagnet $RMnO_3$ and quantum paraelectric $EuTiO_3$, a more realistic model in which a full combination of the ferroelectric and magnetic subsystems is taken into account seems open to us. Katsufuji *et al* [2, 3] found that the change in dielectric and magnetic properties of these materials is dominated by the pair correlation of the nearest-neighbour Mn or Eu ion spins, $\vec{s}_i \cdot \vec{s}_j$. So, for the coupling of intrinsic spin and polarization, we have sufficient reasons for proposing tentatively the form of ME interaction, $gu_k^2\vec{s}_i \cdot \vec{s}_j$, to study theoretically the magnetic and dielectric properties in ferroelectromagnets. In the above ME interaction form, u_k represents the electrical displacement for electrical polarization at site k and $\vec{s}_j$ is the Heisenberg spin for magnetic interaction at site j, where g is a coupling coefficient.

In this paper, we discuss mainly how the intrinsic spin moment and electrical polarization interact with each other by considering the ME effect term $gu_k^2\vec{s}_i \cdot \vec{s}_j$ in the framework of the mean-field approximation and soft mode theory. We also calculate electric polarization p, sublattice magnetic moment s^z, perpendicular ME susceptibility $\chi_{me}^{\perp}$, perpendicular magnetic susceptibility $\chi_m^{\perp}$ and polarization susceptibility χ_p in the absence of an external field and analyse the effect of ME coupling on these physical quantities. We find that an additional electrical polarization is induced by the effect of the magnetic moment, and the

antiferromagnetic transition phase temperature becomes higher due to the effect of electrical polarization. At the same time, polarization induced by magnetic coupling leads to a reduction in the polarization susceptibility χ_p at low temperature.

2. Model and formalism

A three-dimensional cubic ferroelectromagnet system is investigated by using soft-mode theory for a ferroelectric subsystem and the mean-field approximation for a magnetic subsystem, in which there coexists ferroelectric ordering and Néel antiferromagnetic ordering at low temperature. The Hamiltonian of the system can be written as

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

where $\mathcal{H}^e$, $\mathcal{H}^m$ represent the Hamiltonians of the ferroelectric subsystem and the antiferromagnetic subsystem and $\mathcal{H}^{me}$ is the coupling between the two subsystems. Following de Alcantara and Gehring [6] and Janssen [12], $\mathcal{H}^e$, $\mathcal{H}^m$ and $\mathcal{H}^{me}$ may be expressed as, respectively,

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

$$\mathcal{H}^m = \sum_{\langle i,j \rangle} J_1 \vec{s}_i \cdot \vec{s}_j - \sum_{[i,j]} J_2 \vec{s}_i \cdot \vec{s}_j - \sum_i h s_i^x - D \sum_i (s_i^z)^2 \tag{3}$$

$$\mathcal{H}^{me} = \sum_{\langle i,j \rangle, k} g u_k^2 \vec{s}_i \cdot \vec{s}_j - \frac{1}{2} \sum_{[i,j]} (\varepsilon_i + \varepsilon_j) \alpha E (s_i^z s_j^x + s_i^x s_j^z) - \frac{1}{2} \sum_i \varepsilon_i \kappa E (s_i^x s_i^z + s_i^z s_i^x). \tag{4}$$

In equation (2), the $\mathcal{H}^e$ is described by the DIFFOUR model including a potential energy term and a double-well potential. a and b represent the double-well potential parameters, m is the mass, and P_i is the particle momentum at site i. We suppose the displacement u_i is proportional to the local spontaneous polarization p. Moreover, the additional nearest-neighbours electrical interaction and electrical static energy have also been taken into account, U is the polarization interaction coupling parameter and E is the external electric field, which is parallel to the polarization direction. $\langle i, j \rangle$ represents that it is summed once over the nearest neighbours.

The Hamiltonian of the magnetic interaction is studied by a Heisenberg model in equation (3) with antiferromagnetic coupling of the nearest neighbours and ferromagnetic coupling of the next nearest neighbours in the presence of the uniaxial single-ion anisotropy interaction. J_1, J_2 and D represent the antiferromagnetic and ferromagnetic couplings and the single-ion anisotropy constant, respectively. $\vec{s}_i$ is the quantum spin operator at site i. To investigate the perpendicular ME properties, an external magnetic field h is applied in the direction perpendicular to the spin ordered direction z, but in the last of the calculations we take $h = 0$. $[i, j]$ denotes that it is summed once over the next nearest neighbours.

In the Hamiltonian of the ME interaction $\mathcal{H}^{me}$, the first term on the right side denotes the coupling interaction between the electrical and magnetic subsystems, the parameter g is the ME coupling factor and i, j denote the nearest neighbor of site k. The last two terms are the effect of the electric field on the magnetic spin order. Parameters α and κ embody the influence of coupling from the external electric field on spin symmetric exchange and single-ion anisotropy. For two magnetic sublattices a and b, ε_i in equation (4) is determined by which magnetic sublattice i belongs to: $\varepsilon_i = 1$ if i belongs to the first sublattice, $\varepsilon_i = -1$ if i belongs to the second sublattice.

3. Mean-field approximation and soft-mode theory

In our previous paper [13], we found that it is feasible that the mean-field approach may substitute for the spin wave theory within the range of low temperatures in such a ferromagnetoelectric system, even if the spin wave theory is more precise owing to its success in dealing with the dynamic correlation. So, in order to investigate the electric and magnetic properties of a ferroelectromagnetic system, in this section we develop the mean-field approach of the coupling effect and soft-mode theory based on the mean-field approximation for the ferroelectric interaction to the Hamiltonian of equation (1).

At first, for ferroelectric interactions, according to the soft-mode theory based on the mean-field approximation, we can find

$$\begin{aligned}&[-a + 2z_1 g\vec{s}_i \cdot \vec{s}_i + 3b\sigma + bp^2]p = z_1 Up + E\\ &[-a + 2z_1 g\vec{s}_i \cdot \vec{s}_j + 3b(\sigma + p^2)]\sigma = k_B T\end{aligned} \tag{5}$$

where z_1 are the coordinate numbers of the nearest neighbours, k_B is Boltzmann's constant and p is defined by the average of the electrical displacement, that is, $p = \langle u_i \rangle$. σ is the fluctuation of electrical displacement, which is defined by $\sigma = \langle [u_i - p]^2 \rangle$. In order to study dielectric properties, we consider the polarization susceptibility in the presence of spin correlation with their definition. Then

$$\chi_p = (3b(\sigma + p^2) - a - z_1 U + 2z_1 g\langle \vec{s}_i \cdot \vec{s}_j \rangle)^{-1} = \chi_0(1 - \alpha_1 \langle \vec{s}_i \cdot \vec{s}_j \rangle). \tag{6}$$

From the above equation, it is found that the spin correlation has a great influence on χ_p. If we neglect the effect of magnetic orders on p and σ, then $\chi_0 = (3b(\sigma + p^2) - a - z_1 U)^{-1}$ is the polarization susceptibility in the absence of spin correlation and $\alpha_1 = 2z_1 \chi_0 g$ is taken as a coupling factor, i.e. a constant. We can find our theoretical result of χ_p shows a good agreement with the fitted formula of experiment for $YMnO_3$ and $EuTiO_3$ at least in form [2, 3]. We will make a detailed explanation of how χ_p really changes with temperature in the next section.

In the mean-field approximation, then, the Hamiltonian for each spin and ME coupling on sublattice i is reduced to

$$\begin{aligned}\mathcal{H}_i^m + \mathcal{H}_i^{me} = \mathcal{H}_i^a + \mathcal{H}_i^b = &-H_a^x s_{ia}^x - H_a^z s_{ia}^z - D(s_{ia}^z)^2 - \tfrac{1}{2}\kappa E(s_{ia}^x s_{ia}^z + s_{ia}^z s_{ia}^x)\\ &- H_b^x s_{ib}^x - H_b^z s_{ib}^z - D(s_{ib}^z)^2 + \tfrac{1}{2}\kappa E(s_{ib}^x s_{ib}^z + s_{ib}^z s_{ib}^x)\end{aligned} \tag{7}$$

where

$$\begin{aligned}H_a^x &= h - z_1(J_1 + gp^2)\langle s_b^x \rangle + z_2 J_2 \langle s_a^x \rangle + 2\alpha z_2 E\langle s_a^z \rangle\\ H_a^z &= -z_1(J_1 + gp^2)\langle s_b^z \rangle + z_2 J_2 \langle s_a^z \rangle + 2\alpha z_2 E\langle s_a^x \rangle\end{aligned} \tag{8}$$

$$\begin{aligned}H_b^x &= h - z_1(J_1 + gp^2)\langle s_a^x \rangle + z_2 J_2 \langle s_b^x \rangle - 2\alpha z_2 E\langle s_b^z \rangle\\ H_b^z &= -z_1(J_1 + gp^2)\langle s_a^z \rangle + z_2 J_2 \langle s_b^z \rangle - 2\alpha z_2 E\langle s_b^x \rangle.\end{aligned} \tag{9}$$

Here $\langle \cdots \rangle$ is the sublattice magnetization which represents the thermal average of the expectation value of the Heisenberg spin along the direction z and x, respectively, and z_2 are the coordinate numbers of the next nearest neighbours. H_a^i and H_b^i are the effective fields acting on the two sublattices in different directions. According to statistical physics, the thermodynamic averaging of the physical quantities $\langle s_a^x \rangle$, $\langle s_a^z \rangle$, $\langle s_b^x \rangle$ and $\langle s_b^z \rangle$ can be expressed by using the following solutions in the case of $s = 1$:

$$\langle s_l^x \rangle = -k_B T \frac{\partial}{\partial(-H_l^x)} \ln \mathrm{Tr} \exp(-\beta \mathcal{H}_i^l) \tag{10}$$

$$\langle s_l^z \rangle = -k_B T \frac{\partial}{\partial(-H_l^z)} \ln \mathrm{Tr} \exp(-\beta \mathcal{H}_i^l) \tag{11}$$

where $l = a, b$. Then the other quantities can be obtained:

$$m^x = \sum_{i=a,b} \langle s_i^x \rangle \tag{12}$$

$$m^z = \sum_{i=a,b} \langle s_i^z \rangle \tag{13}$$

$$\chi_m^{\perp} = \frac{\partial m^x}{\partial h} = \lim_{\Delta h \to 0} \frac{\Delta m^x}{\Delta h} \tag{14}$$

$$\chi_{me}^{\perp} = \frac{\partial m^x}{\partial E} = \lim_{\Delta E \to 0} \frac{\Delta m^x}{\Delta E}. \tag{15}$$

4. Results and discussions

The electrical polarization p, thermal fluctuation of electrical displacement σ and thermodynamic average values of spin moment $\langle s_a^x \rangle$, $\langle s_a^z \rangle$, $\langle s_b^x \rangle$ and $\langle s_b^z \rangle$ via temperature can be obtained by the self-consistent equations (5), (10) and (11), respectively. In the light of [10, 11] and the case of real perovskite-type crystals, the parameters used in our calculation are: $z_1 = 6$, $z_2 = 12$, $J_1 = 0.4$, $J_2 = 0.15$, $D = 0.1$ for a cubic antiferromagnetic system, $a = 1.5$, $b = 3.0$, $U = 1.5$ for a ferroelectric double-potential well and $g = 0.05$–0.1, $\alpha = 0.1$, $\kappa = 0.1$ for the ME coupling interaction, but these parameters must be met with $T_N < T_E$, where T_N is the Néel point of the antiferromagnetic order and T_E is the Curie point of the ferroelectric transition.

The polarization p and polarization susceptibility χ_p as a function of temperature are shown in figures 1 and 2, in which the coupling coefficient g is given as 0.05, 0.08 and 0.1. It is shown that p decreases with the increase in temperature. This is because increasing the temperature leads to a disorder in the ferroelectric polarization order. For the different ME couplings, nevertheless, it changes not only the antiferromagnetic order phase transition temperature T_N but also the value of the ferroelectric polarization at a certain temperature below T_N. This can be explained from the term of the ME coupling interaction. Because of the effect of the pair correlation of the nearest-neighbours ionic spin, the double-well potential parameter was modified from $-a/2$ to $-a/2 + g\langle \vec{s}_i \cdot \vec{s}_j \rangle$. The two potential wells become deeper, that is, it is more difficult for a particle to tunnel between them, so the electric polarization p becomes correspondingly stronger. Moreover, the ME coupling g is larger, so the value of p also becomes larger at very low temperatures, as shown in figure 1. At the same time, from figure 2, we also find that the ME effect leads to an anomaly in χ_p calculated from equation (6) near T_N, which is qualitatively consistent with that of experiments [1, 4] carried out on ferroelectromagnets. From equation (6), it seems that χ_p will be larger below T_N due to antiferromagnetic correlation. In fact, increasing p caused by antiferromagnetic correlation will lead to χ_0 decreasing. The final result is that a decreasing χ_p occurs over the whole temperature range below T_N. With an increase of the ME coupling g, the decrease in the curves of $\chi_p \sim k_B T$ appears more explicit. Therefore, we can deduce the occurrence of dielectric anomalies have much to do with the coupling between the ferroelectrics and the correlation of the spin.

In figures 3 and 4, the variations of the spin moment $\langle s_i^z \rangle$, and perpendicular magnetization susceptibility $\chi_m^{\perp}$ in the absence of an external field with temperature are given, in which the value of the ME coupling coefficient g is the same as that used previous. It is shown that ME coupling changes only the antiferromagnetic order phase transition temperature T_N, which is different from that of the effect of an external electric field. Under the effect of an applied electric field perpendicular to the spin alignment, as studied in [6], however, each sublattice

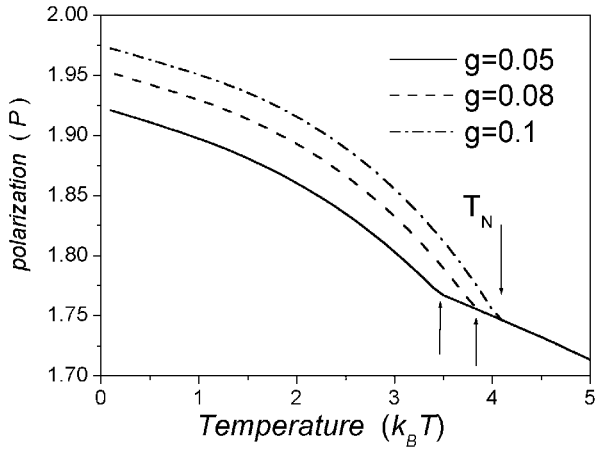

Figure 1. Temperature dependence of the polarization p for different ME coupling constants, g.

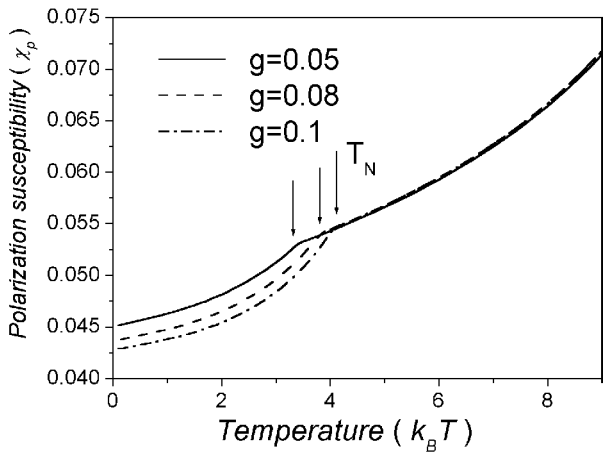

Figure 2. Temperature dependence of the polarization susceptibility χ_p for given ME coupling constant, g.

spin will rotate symmetrically towards the x direction, and the value of $\langle s^z \rangle$ in the sublattice will decrease correspondingly at a certain temperature. In our coupling mechanism, it is easy to see that the coupling modified the exchange interaction J_1 of the nearest neighbours to $J_1 + gp^2$. Accordingly, although T_N has an obvious higher trend when perpendicular ME coupling becomes stronger, the value of $\langle s^z \rangle$ is still constant at the ground state. This can also be noted in figure 4 for the curve of $\chi_m^{\perp}$, in which the effect of the ME coupling on T_N is very explicit. As well as on χ_p, in addition, the ME coupling results in a decrease in the magnetization susceptibility $\chi_m^{\perp}$. Such a decrease is also very obvious for the temperatures below T_N when the ME coupling was strengthened.

Figure 5 exhibits the variation of the perpendicular ME susceptibility $\chi_{me}^{\perp}$ as a function of temperature, which is found be consistent with that of phenomenological theory [14] and statistical theory [15]. In these theories, the relation between $\chi_{me}^{\perp}$, $\chi_m^{\perp}$ and $\langle s^z \rangle$ was found to satisfy $\chi_{me}^{\perp} \propto \chi_m^{\perp} \langle s^z \rangle$, that is, $\chi_{me}^{\perp}$ is proportional to the product of $\chi_m^{\perp}$ and $\langle s^z \rangle$. In order to compare them with our mean-field result, by combining figures 3 and 4 it is seen that, as the

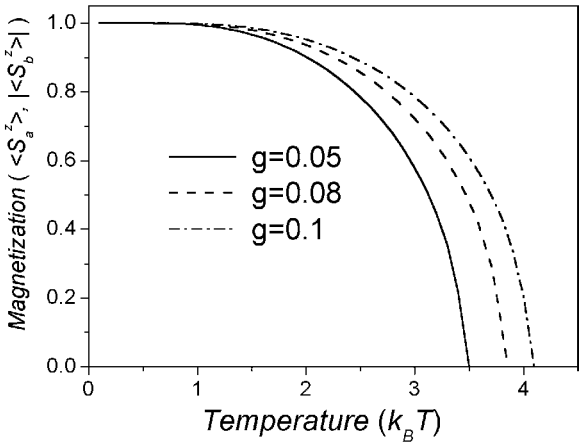

Figure 3. Temperature dependence of the sublattice magnetization $\langle S_a \rangle$ and $|\langle S_b \rangle|$ for different ME coupling coefficients, g.

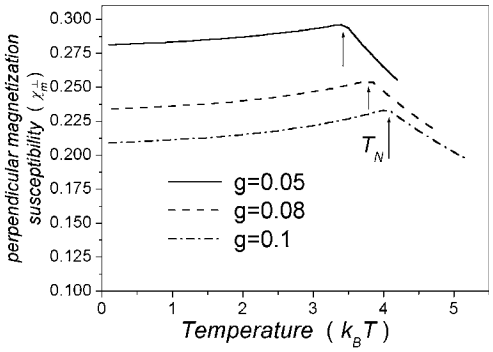

Figure 4. Temperature dependence of the perpendicular magnetic susceptibility $\chi_m^{\perp}$ for a given ME coupling constant, g.

temperature $k_B T$ increases from 0 K to the Néel temperature, T_N, the quantity $\chi_{me}^{\perp}$ decreases monotonically from some finite value to zero in the manner of the sublattice magnetization, which is in agreement with our conclusion as shown in figure 5. In addition, the quantity $\chi_{me}^{\perp}$ becomes smaller at very low temperatures because of the effect of $\chi_m^{\perp}$, while the ME coefficient g becomes larger, and T_N shifts towards higher temperatures, which has been analysed.

5. Conclusion

An attempt has been made to understand the electrical, magnetic and ME properties of ferroelectromagnetic systems in which antiferromagnetic and ferroelectric order coexist spontaneously at low temperatures. By considering a coupling form of $gu_k^2 \vec{s}_i \cdot \vec{s}_j$ and combining the soft-mode theory for ferroelectric order and the mean-field theory for antiferromagnetic order, we have calculated thermodynamic properties of the system, including magnetization, polarization, magnetization susceptibility, ME susceptibility and polarization susceptibility, in the case of magnetization perpendicular to polarization. Because the experimental studies have shown that the ferroelectric order is perpendicular to the magnetic order at the ground state

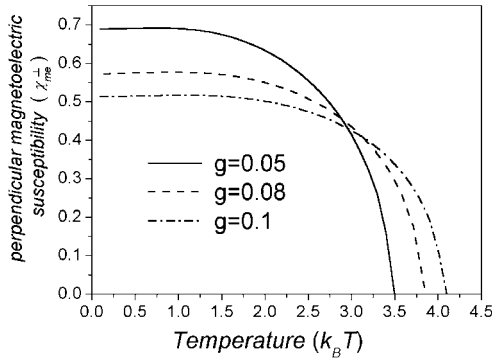

Figure 5. Temperature dependence of the perpendicular ME susceptibility $\chi_{me}^{\perp}$ for different ME coupling constants, g.

in most perovskite-type structure ferroelectromagnets, if we describe the ME coupling by an Ising model, it will be too simple for the condition that the anisotropic energy is not too strong. It is also found that the relation between magnetization, magnetization susceptibility and ME susceptibility is in good agreement with that of the phenomenological theory. In addition, polarization induced by magnetic coupling leads to an decrease in polarization susceptibility over the whole range of temperature below T_N. This is in qualitative agreement with the results of the recent experiment. Thus it can be seen that the occurrence of a dielectric anomaly in ferroelectromagnetic matter has much to do with the coupling between spin correlation and electrical polarization.

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