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Microfields Induced by Random Compensated Charge Pairs in Ferroelectric Materials

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ABSTRACT

The dc and microwave responses of the $Ba_xSr_{1-x}(X,Y)_yTi_{1-y}O_3$ family of ferroelectric compounds with various substitutional additives X^{3+}, Y^{5+} are analyzed by combining the random-field technique with the mean-field (Landau-Devonshire) theory of ferroelectricity, along with a self-consistent computation of the dielectric constant of the host material in the presence of the impurity fields. The fields in the material are assumed to arise from charge compensation at the Ti^{4+} sites, leading to permanent dipoles made up of the resulting positive and negative ions separated by a few lattice constants. It is shown that whereas completely random placement of positive and negative ions generates a Holtsmark distribution of electric field, with infinite second moment and hence extremely large fluctuations in field strength, the association of ionized impurities into permanent dipoles leads to much lower fluctuations in field and a distribution with finite second moment, which makes a self-consistent dielectric constant meaningful.

INTRODUCTION

The usefulness of ferroelectric materials in the design of electronic devices arises from the ease with which their electrical characteristics, e.g., conductivity, dielectric constant, optical birefringence, etc., can be controllably modified so as to produce a desired functionality. A standard way of controllably modifying a material is to introduce foreign elements into a host material at concentrations that are too low to change its intrinsic chemical nature, but which modify its behavior at the macroscopic level. In ferroelectrics, these modifications are usually associated with the presence of built-in electric fields, which are generated by thermal ionization of the added impurity atoms. This type of processing is well known in the semiconductor industry, where materials are routinely "doped" to make them conductive and otherwise electrically active.

However, because semiconductors already contain large amounts of free, i.e., mobile, charge, it is normally assumed that there are no macroscopic fields inside them. Because doping such materials with impurities creates ionized donor and acceptor centers in addition to the free charge, it would seem that long-range fields should appear. However, the free charge can move to screen out any such fields [1] over distances that are larger than the Debye length in the bulk:

$$l_D = \sqrt{\frac{\varepsilon kT}{ne^2}} = 120\sqrt{\frac{\varepsilon}{n}} \text{ cm at room temperature,} \qquad (1)$$

where n is the carrier density, ε the dielectric constant. For $n \approx 10^{12}$ cm^{-3} , which is a lower limit on how low the free charge can be in most semiconductors, this gives $l_D \approx 1.2$ μm, i.e., very small. Over these distances the fields can only create small potential fluctuations, which modulate the bottom of the material conduction band to produce so-called "bandtails", as shown long ago by Evan Kane [2] and Halperin and Lax [3]. In contrast, insulating materials can have vanishingly small amounts of free charge in their interiors, and hence can sustain long-range fields. Although these fields will vary randomly in magnitude and direction, they can superimpose and become quite large. In this paper we develop a statistical method to calculate the behavior of fields associated with charged impurities in ferroelectrics, and use it to discuss the effect these fields have on the host material's dielectric response.

FIELD PROBABILITY DISTRIBUTIONS

The appropriate description of random electric fields in an insulator is statistical, since the added charge centers are located randomly throughout the material bulk. This means that at any given point in the material we can assume that there is a probability distribution for the field, i.e., that the field is a random variable. The usefulness of this picture depends on what observable we plan to calculate. If the observables of interest involve volume averages, these can be evaluated conveniently by invoking the ergodic hypothesis, i.e., we can replace the volume average by an ensemble average. To proceed beyond this point the probability distribution of the quantity being averaged is required.

We begin by calculating the probability distribution for electric fields generated by one species of added impurity. If the impurity centers are uniformly distributed, then the probability $p_I(\vec{x})$ that there is an impurity at position $\vec{x}$ is simply $1/V$, where V is the host volume. To find the field distribution we use a method pioneered by Markov [4], discussed first in the astronomy literature by Holtsmark [5] and then in the astrophysics literature by Chandrasekhar [6], and finally in solid state by P. W. Anderson [7] to discuss electron localization in disordered media and by Stoneham [8] to discuss optical line shapes. First, we note that if the impurity positions $\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots$ are random vector variables with probability distributions $p_1(\vec{x}_1), p_2(\vec{x}_2), p_3(\vec{x}_3), \dots$, and $\vec{f} = \vec{f}(\vec{x}|\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots)$ is some vector function of these variables and the position $\vec{x}$ of a point in the solid, then $\vec{f}$ is a random variable with a probability density given by the expression

$$P(\vec{f}(\vec{x}) = \vec{f}_0) = \left\langle \delta(\vec{f}_0 - \vec{f}(\vec{x}|\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots)) \right\rangle = \int \prod_{n=1}^{N} p_n(\vec{x}_n) d\vec{x}_n \delta(\vec{f}_0 - \vec{f}(\vec{x}|\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots)) \quad (2)$$

In our specific case, $\vec{f}$ will be the field due to the random charges.
Using the exponential representation of the δ-function

$$\delta(\vec{x}) = \int_{-\infty}^{\infty} e^{i\vec{q}\cdot\vec{x}} \frac{d^3q}{(2\pi)^3} \quad (3)$$

we can write the following expression for the density P associated with the overall probability that the electric field $\vec{E}_I$ due to the charged impurities has a value $\vec{E}$ at the point $\vec{x}$:

$$P(\vec{E}_I(\vec{x})=\vec{E}) = V^{-2N}\int\prod_n d\vec{x}_n \int_{-\infty}^{\infty} \exp[i\vec{q}\cdot\{\vec{E}-\vec{E}_I(\vec{x}|\vec{x}_1,\vec{x}_2,\vec{x}_3,...)\}]\frac{d^3q}{(2\pi)^3} \qquad (4)$$

Uncorrelated Positive and Negative Monopoles

Assume now that we put an equal number N of positive and negative charges ("donors" and "acceptors" in semiconductor language) into the material, so that it is electrically neutral (charge-compensated). Let these charges be at locations $\vec{x}_{D1},\vec{x}_{D2},\vec{x}_{D3},...\vec{x}_{A1},\vec{x}_{A2},\vec{x}_{A3},...$, with probability densities $p_{Dj}(\vec{x}_{Dj}), p_{Aj}(\vec{x}_{Aj})$ that are uniform and uncorrelated as asserted above, i.e., $p_{Dj}(\vec{x}_{Dj}) = p_{Aj}(\vec{x}_{Aj}) = \frac{1}{V}$.

Then the function $\vec{E}_I(\vec{x}|\vec{x}_1,\vec{x}_2,\vec{x}_3,...)$ has the form

$$\begin{aligned} \vec{E}_I(\vec{x}|\vec{x}_{D1},\vec{x}_{D2},...,\vec{x}_{A1},\vec{x}_{A2},...) &= \nabla \sum_{j=1}^{N} \frac{e}{|\vec{x}-\vec{x}_{Dj}|} - \frac{e}{|\vec{x}-\vec{x}_{Aj}|} \\ &= \sum_{j=1}^{N} \vec{E}(\vec{x}-\vec{x}_{Dj}) - \vec{E}(\vec{x}-\vec{x}_{Aj}) \end{aligned} \qquad (5)$$

where $\vec{E}(\vec{x}) = e\frac{\vec{x}}{\varepsilon|\vec{x}|^3}$ is the electric field of a point charge and ε is the relative permittivity of the host material. Then Eq. (1) can be rewritten as follows:

$$P(\vec{E}_I(\vec{x})=\vec{E}) = \int_{-\infty}^{\infty} \exp[i\vec{q}\cdot\vec{E}]\frac{d^3q}{(2\pi)^3}\left(V^{-1}\int\exp[-i\vec{q}\cdot\vec{E}(\vec{x})]d\vec{x}\right)^N \left(V^{-1}\int\exp[i\vec{q}\cdot\vec{E}(\vec{y})]d\vec{y}\right)^N \qquad (6)$$

If the densities of donors and acceptors are $n_D = n_A \equiv n$, we can write $V = n/N$. Using this notation, we have that

$$\left(V^{-1}\int\exp[-i\vec{q}\cdot\vec{E}(\vec{x})]d\vec{x}\right)^N = \left(1-V^{-1}\int\{1-\exp[-i\vec{q}\cdot\vec{E}(\vec{x})]\}d\vec{x}\right)^N \qquad (7)$$

This lets us write [9]

$$P(\vec{E}_I(\vec{x})=\vec{E}) = \int_{-\infty}^{\infty} \exp[i\vec{q}\cdot\vec{E}]\exp[-2n\,\mathrm{Re}\,F(\vec{q})]\frac{d^3q}{(2\pi)^3} \qquad (8)$$

Now, the integral

$$\mathrm{Re}\,F(\vec{q}) = \int\{1-\cos[\vec{q}\cdot\vec{E}(\vec{x})]\}d\vec{x} \qquad (9)$$

reduces the function P to Holtsmark's distribution (see Ref. [5]) with a total density of carriers $2n$. Some manipulation gives

$$\mathrm{Re}\,F(\vec{q}) = \frac{4}{15}(2\pi)^{3/2} e^{3/2} |q|^{3/2} \tag{10}$$

which implies a distribution of the form

$$P(\vec{E}_I(\vec{x}) = \vec{E}) = \int_{-\infty}^{\infty} \exp[i\vec{q}\cdot\vec{E} - \sigma|\vec{q}|^{3/2}] \frac{d^3 q}{(2\pi)^3} \tag{11}$$

where $\sigma = \frac{8}{15}(2\pi)^{3/2} n e^{3/2} = 8.400 n e^{3/2}$ is a scale factor with dimensions $[\text{field}]^{3/2}$. This reduces to the 1D integral of Holtsmark

$$P(\vec{E}_I(\vec{x}) = \vec{E}) = \frac{1}{2\pi^2 |\vec{E}|^3} \int_0^{\infty} \exp[-\sigma x^{3/2} / |\vec{E}|^{3/2}] x \sin x\, dx \tag{12}$$

which cannot be reduced further.

If the host material has a lattice constant a, we can write $n = ca^{-3}$, where c is the impurity concentration (dimensionless). Then $\sigma = 8.400c\left(\frac{e}{\varepsilon a^2}\right)^{3/2}$ introduces a scaling electric field $E_{sc} = \frac{e}{\varepsilon a^2}$ into the problem, in terms of which $\sigma = 8.400cE_{sc}^{3/2}$. Taking a = 4 Å and $\varepsilon = 1000$, which are typical values for ferroelectrics, we find that this field is about 110 V/μm, i.e., close to breakdown of the material.

Fully dipole-correlated charge distributions

Suppose now that every donor is spatially paired with an acceptor, i.e., is physically separated from it by only a few lattice constants. The resulting pairs of charges can then be treated as unit sources of random electric field, i. e., dipoles. At low carrier concentrations (so that the dipoles are far apart) we can treat the fields of these dipoles as we did the fields above. Now, however, the field $\vec{E}(\vec{x}) = e^2 \frac{\vec{x}}{\varepsilon|\vec{x}|^3}$ is replaced by the field of a dipole, i.e., a field of the form

$$\vec{E}(\vec{x}) = \wp \frac{3\vec{x}(\vec{x}\cdot\hat{n}) - x^2\hat{n}}{\varepsilon|\vec{x}|^5} \tag{13}$$

where $\hat{n}$ gives the direction of the dipole and $\wp$ its strength. For a cubic crystal the dipole direction can vary in 6 cubic directions for nearest neighbors and 8 for next nearest neighbors. Let us ignore the discreteness of the possible orientations and suppose that $\wp$ is a constant vector that can point in any direction, i.e., the Heisenberg problem. Then we can replace the sum by an angular average:

$$\begin{aligned} &V^{-1}\int \exp[-i\vec{q}\cdot\vec{E}(\vec{x})]d\vec{x} \to V^{-1}\frac{1}{4\pi}\int d\hat{n}\int \exp[-i\vec{q}\cdot\vec{E}(\vec{x})]d\vec{x} \\ &= V^{-1}\int d\vec{x}\,\frac{1}{4\pi}\int \exp\left[-i\frac{\wp}{|\vec{x}|^{3}}\vec{q}\cdot\vec{J}(\vec{x})\right]d\hat{n} \equiv \int < S > d\vec{x} \end{aligned} \tag{14}$$

where

$$\vec{J} = 3\hat{n}(\hat{n}\cdot\hat{q}) - \hat{q}\,. \tag{15}$$

Considerable manipulation eventually gives the result

$$P(\vec{E}_I(\vec{x}) = \vec{E}) = \int_{-\infty}^{\infty} \exp[i\vec{q}\cdot\vec{E} - n\gamma|\vec{q}|]\frac{d^3q}{(2\pi)^3} \tag{16}$$

where $\gamma = \frac{\pi^2\wp}{3}\left(1 + \frac{\sinh^{-1}\sqrt{3}}{2\sqrt{3}}\right) \approx 5.89\wp$. Unlike the Holtsmark distribution, this expression can be evaluated in closed form, leading eventually to the result

$$P(\vec{E}_I(\vec{x}) = \vec{E}) = \frac{\gamma n}{\pi^2}\frac{1}{\left(E^2 + \gamma^2 n^2\right)^2} \tag{17}$$

which appears in the work of Ma [10]. Again, a scaling field enters into the problem: if we take the dipole moment to equal *ea*, where *a* is the lattice constant, this field is once more $E_{sc} = \frac{e}{\varepsilon a^2}$, where now we write $\gamma n = 5.89cE_{sc}$.

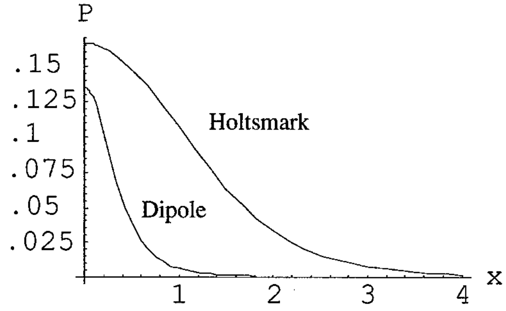

Figure 1. Holtsmark and dipole distributions. The dipole curve is scaled by a factor of 1/100.

Figure 1 shows a numerical plot of this function, together with the Holtsmark distribution, for the same lattice constant and scaling field. Note that both these functions are centered around zero, since they are vector distributions and there is no preferred direction in the crystal. For convenience purposes the functions plotted are actually $2\pi^2\sigma^2 P_H(x)$ and $2\pi^2\sigma^2 P_D(x)$, where $x = \frac{E}{\sigma^{2/3}}$, since the Holtsmark function $2\pi^2\sigma^2 P_H(x)$ is a universal function in this coordinate. In contrast, the dipole function $2\pi^2\sigma^2 P_D(x)$ takes the form $\frac{2\Gamma}{\left(x^2 + \Gamma^2\right)^2}$, where Γ is a function only of the concentration: $\Gamma = 1.43\, c^{1/3}$. The dipole plot shown is for $c = .05$, on a scale reduced by a factor of 100. Note that the Holtsmark distribution is much broader than the dipole distribution, with a longer tail. This difference is a manifestation of the long range of the Coulomb interaction, and in fact causes the Holtsmark distribution to have no second moment – i.e., the fluctuations are so large that their mean square deviation from the average field is infinite! In contrast, the dipole distribution has finite fluctuations, although it, too, is somewhat badly behaved, having no moments *higher* than the second.

THERMODYNAMIC VARIABLES

Let us characterize the ferroelectric by using the Landau-Devonshire theory [11]. In this picture, the properties of the ferroelectric near the Curie temperature are determined by its free energy, which is of the form

$$F = -\vec{E}\cdot\vec{D} + \frac{1}{2}a(T)D^2 + \frac{1}{4}bD^4 + \frac{1}{6}cD^6 \tag{18}$$

where D is the displacement, E denotes an external electric field, and a, b, and c are material parameters. We will assume here that (1) the material undergoes a second-order phase transition at T_C, which requires that $c = 0$, $b > 0$, and (2) that only a depends on temperature, specifically that $a(T) = \alpha(T - T_C)$, where T_C is the Curie temperature. Then the relation between the displacement $\vec{D}$ and the electric field $\vec{E}$ is found by minimizing the free energy with respect to the *vector* $\vec{D}$:

$$\frac{dF}{dD_i} = -E_i + \left[a(T) + bD^2\right]D_i = 0 \tag{19}$$

Normally we would just solve this equation for $\vec{D}$, but here the field $\vec{E}$ is a random variable so that a different approach is needed. If we assume that the crystal is isotropic, then the vectors $\vec{D}$ and $\vec{E}$ are always parallel and $\vec{D} = D\hat{n}$ where $\hat{n}$ is the direction of the field $\vec{E}$. Then

$$\vec{D} = \frac{1}{a + bD^2}\vec{E} \Rightarrow D = \frac{1}{a + bD^2}\left|\vec{E}\right| \equiv \frac{1}{a + bD^2}E \tag{20}$$

where E is the magnitude of $\vec{E}$. This implies that

$$E^2 = \left(a + bD^2\right)^2 D^2 \tag{21}$$

In the presence of an applied field $\vec{E}_a$, the average displacement is given by

$$< D_i >= \int D_i(\vec{E}) P(\vec{E} - \vec{E}_a) d^3E = \frac{E_f}{\pi} \int D_i(\vec{E}) \frac{d^3E}{\left(E_f^2 + \left|\vec{E} - \vec{E}_a\right|^2\right)^2} \tag{22}$$

where $E_f = \gamma n = 5.89\left(\frac{e}{\varepsilon a^2}\right)c$ is the "width" of the field fluctuation distribution. Note that the distribution is now centered around the deterministic external field $\vec{E}_a$.

Dielectric constant

Let us introduce the variable $x \equiv D^2$. Then $E^2 = x(a + bx)^2$ and $D = \frac{1}{a + bx} E$.

If the z – axis points along the applied field and we write $d^3E = 2\pi E^2 dE d\xi$, where $\xi = \cos\theta$ depends on the angle between the integration field and the applied field, the integral becomes

$$\begin{aligned} < D >=< \hat{n}_a \cdot \vec{D} > &= \frac{E_f}{\pi^2} \int_0^\infty \frac{E}{a + bx} 2\pi E^2 dE \int_{-1}^{1} \frac{\xi d\xi}{\left(E_f^2 + E_a^2 + E^2 - 2EE_a\xi\right)^2} \\ &= \frac{2E_f}{\pi} \int_0^\infty \frac{E^3 dE}{a + bx} \int_{-1}^{1} \frac{\xi d\xi}{\left(E_f^2 + E_a^2 + E^2 - 2EE_a\xi\right)^2} \end{aligned} \tag{23}$$

For small external fields we can expand the angular integrand in a power series. Then the angular integrations are trivial, and we end up with

$$\begin{aligned} < D >&= \frac{2E_f}{\pi} \int_0^\infty \frac{E^3 dE}{a + bx} \left\{ \frac{8E}{3\left(E_f^2 + E^2\right)^3} E_a + \frac{8E\left(-5E_f^2 + 3E^2\right)}{5\left(E_f^2 + E^2\right)^5} E_a^3 + \cdots \right\} \\ &= \varepsilon E_a + \beta E_a^3 + \cdots \end{aligned} \tag{24}$$

where ε and β are the dielectric constant and tunability of the material. Near the Curie point we can set $a = 0$, which simplifies the relation between E and x to $E = bx^{3/2}$. This in turn simplifies the integrals, and we find that

$$\varepsilon = \frac{14}{27} E_f^{-2/3} b^{-1/3} \qquad \beta = -\frac{14}{729} E_f^{-8/3} b^{-1/3} \tag{25}$$

Self-consistency

In the spirit of mean-field theory we now specify that the dielectric constant used to determine the field fluctuation width E_f be the same as the one we calculate from the macroscopic theory, i.e., $E_f = 5.89\left(\frac{e}{\varepsilon a^2}\right)c$. At the Curie temperature, however, we know from the previous section that $\varepsilon = \frac{14}{27\left(E_f^2 b\right)^{1/3}}$, from which we obtain $\left(\frac{E_f}{b}\right)^{1/3} = \frac{11.36ec}{a^2}$. Solving this for E_f gives $E_f = 1466\left(\frac{ec}{a^2}\right)^3 b$. Then $\varepsilon(T_C) = 5.89\left(\frac{ec}{a^2}\right)\frac{1}{E_f} = .004\left(\frac{ec}{a^2}\right)^{-2}\frac{1}{b}$, i.e., the peak in ε is $\propto c^{-2}$. Since the fluctuation width is affected by the external field E_a, calculating the tunability requires some care. If $\varepsilon = \varepsilon_0\left(E_f\right) + \beta\left(E_f\right)E_a^2$, we apply self-consistency in the following form:

$$\varepsilon\left(E_f\right)E_f = 5.89\left(\frac{ec}{a^2}\right) \equiv C_0 \Rightarrow \varepsilon\left(E_f\right) = \frac{C_0}{E_f} \tag{26}$$

Writing the width as $E_f = E_{f0} + \lambda E_a^2$ and equating powers of E_a^2 gives a zero-order equation

$$\varepsilon_0\left(E_{f0}\right) = \frac{C_0}{E_{f0}} \tag{27}$$

and a first-order equation

$$\lambda = -\frac{\beta\left(E_{f0}\right)E_{f0}^2}{C_0 + \varepsilon_0'\left(E_{f0}\right)E_{f0}^2} \tag{28}$$

If $\varepsilon = \varepsilon_0\left(E_f\right) + \tilde{\beta}\left(E_f\right)E_a^2$, then

$$\tilde{\beta}\left(E_{f0}\right) = -\lambda\frac{C_0}{E_{f0}^2} = 3\beta\left(E_{f0}\right) = -\frac{14}{243}E_f^{-8/3}b^{-1/3} \tag{29}$$

At low concentrations we find that the tunability is $\propto c^{-8}$, i.e., a very strong function of c.

Numerical Results

In order to deal with finite temperatures we must allow a to be nonzero, which complicates the analysis. Making the integration variable change $E^2 = x(a+bx)^2$ and $D = \frac{1}{a+bx}E$ leads to the following expression for the average displacement:

$$< D >=< \hat{n}_a \cdot \vec{D} >= \frac{2E_f}{\pi} \int_0^\infty x^{3/2}(a+bx)^3(a+3bx)dx \cdot \int_{-1}^{1} \frac{\xi d\xi}{\left(E_f^2 + E_a^2 + x(a+bx)^2 - 2E_a x^{1/2}[a+bx]\xi\right)^2} \qquad (30a)$$

The angular integral can be carried out easily, but it leads to an awkward expression. Again it is clear that $< D >$ vanishes as $E_a \to 0$. It is possible to modify the theory slightly to obtain the behavior of the material below the Curie temperature as well, from the integral

$$< D >= \frac{2E_f}{\pi} \int_{|a|/b}^\infty x^{3/2}(-|a|+bx)^3(-|a|+3bx)dx \int_{-1}^{1} \frac{\xi d\xi}{\left(E_f^2 + E_a^2 + x(-|a|+bx)^2 - 2E_a x^{1/2}[-|a|+bx]\xi\right)^2} \qquad (30b)$$

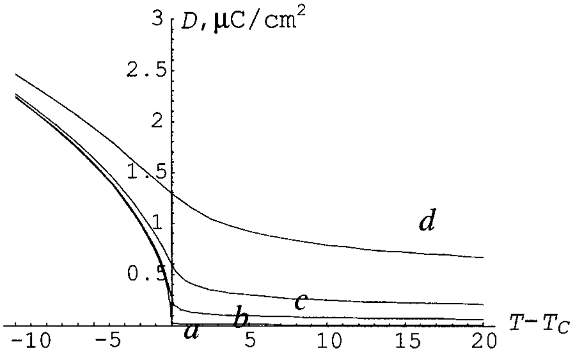

Figure 2. Spontaneous displacement versus temperature for BaSrTiO$_3$ with +3 and +5 ions added. Impurity concentrations: (*a*) 0.0001, (*b*) 0.001, (*c*) 0.01, and (*d*) 0.1.

Numerical evaluation of $< D >$ leads to the curves shown in Fig. 2. We find the low-field dielectric constant by linearizing in E_a, which yields:

$$\varepsilon = \frac{8E_f}{3\pi}\int_0^{\infty}\frac{x^{3/2}(a+bx)^3(a+3bx)dx}{\left(E_f^2+x(a+bx)^2\right)^3}, \qquad T > T_C \qquad (31a)$$

$$= \frac{8E_f}{3\pi}\int_{|a|/b}^{\infty}\frac{x^{3/2}(-|a|+bx)^3(-|a|+3bx)dx}{\left(E_f^2+x(-|a|+bx)^2\right)^3}, \qquad T < T_C \qquad (31b)$$

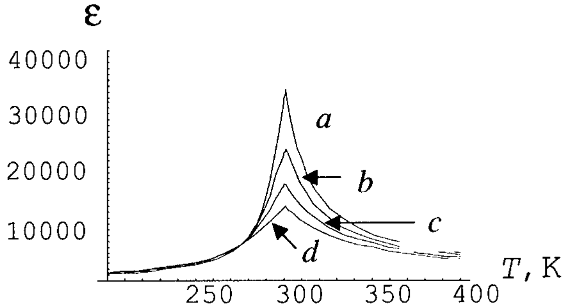

Figure 3. Dielectric constants vs. temperature for dipole-doped $BaSrTiO_3$. Concentrations: (*a*) 0.005 , (*b*) 0.006 , (*c*) .007 , (*d*) .008.

Self-consistency was imposed numerically on these functions to obtain the curves shown in Fig. 3. The results are within an order of magnitude of what we typically observed in experiments. However, these theoretical curves do not predict the experimentally observed shift in the Curie temperature with concentration [12].

CONCLUSIONS

In light of the crudeness of this theory, it is unlikely that it will be very predictive when applied to real $(Ba_xSr_{1-x})(X,Y)TiO_3$ systems, for a number of reasons: the actual phase transitions in these materials are first order, they are ceramics, etc. Including these phenomena will require at a minimum the use of a version of the Landau-Devonshire theory with $c \neq 0$, making the analysis more complex.

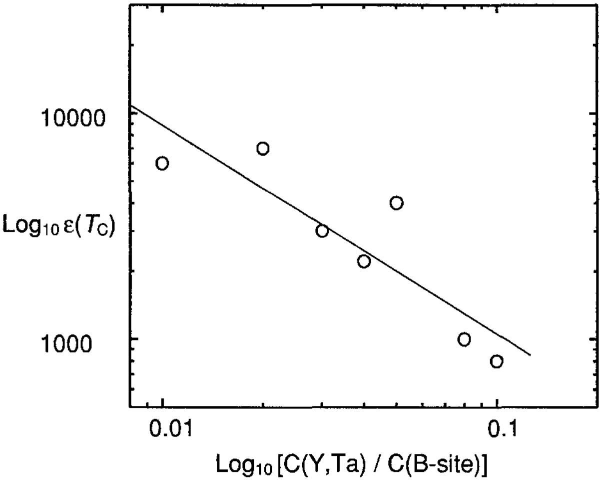

Figure 4. Peak dielectric constant vs. concentration. A least-squares fit gives

$$\mathrm{Log}_{10}\,\varepsilon(T_C) = 2.1 - .92\,\mathrm{Log}\left(\frac{c_{Y,Ta}}{c_{B-site}}\right).$$

As an example of the disagreement between theory and experiment, Fig. 4 shows the concentration dependence of the dielectric constant peak for members of the material set $(Ba_xSr_{1-x})(Y,Ta)_yTi_{1-y}O_3$. In contrast to the slope of -2 predicted by theory, a slope close to -1 is observed [13]. It is worth noting that all these materials had different grain sizes, and that the Curie temperature was different for every data point shown. This suggests that the correct dependence will only be derived when the theory can predict concentration-induced changes in T_C as well. We hope to explore this issue in a future publication.

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