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Investigation of a relationship between dielectric peak diffuseness and elastic modulus variations in a ferroelectric relaxor

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The dependence with temperature of elastic modulus of relaxor ferroelectric ceramics is modeled with a Landau-Devonshire-type cluster theory. The effective elastic modulus obtained from experimental data of ultrasonic longitudinal velocity in PCT and PLZT ferroelectric ceramics are compared with the proposed model. This comparison shows that the model is able to reproduce the dependence with temperature of elastic modulus c very well. We obtained that as impurity concentration increases in both families, the diffuseness of the transition shows important variations, but the strengths of the couplings between the polarization and the strain remain almost unchanged. In contrast, other models assigned a change in the strengths of the couplings between the polarization and the strain to explain the diffuse transition in these compounds. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4869200>]

I. INTRODUCTION

As it is well known, ultrasonic velocity and attenuation are very useful to obtain information about ferroelectric properties.¹⁻⁴ Although ultrasound is sensitive to dielectric mechanisms, it has the advantage of also providing information of associated mechanical mechanisms. To analyze the results of ultrasonic velocity, the equation of Rehwald is typically used,⁵ together with a phenomenological equation for the dielectric constant.^{2,3} This leads to an equation relating elastic modulus, coupling between polarization and strain, polarization, and diffuseness.

To apply this equation, the polarization must be described as a function of the temperature. The quadratic interaction between the strain S and the polarization P is usually neglected, to disregard the description of polarization above T_m , which is a priori unknown. Within this approximation, useful information can be obtained related with the diffuseness of the transition. However, this procedure may introduce an error since P is not zero above T_m . In addition with this method, we cannot study the coupling dependence with temperature around the transition temperature. To avoid this problem, in this paper, we used a description that allows us to obtain the polarization; and consequently, the linear and nonlinear terms in the S - P coupling can be included in the fittings in a temperature range around T_m . In doing so, we shall employ a cluster model combined with the Landau-Devonshire free energy.^{6,7}

It is believed that the broadening of the ferroelectric relaxor transition is caused by inhomogeneity of chemical composition or disorder in the distribution of ions (compositional disorder).⁸⁻¹⁰ Thus, it is currently accepted that the relaxor ferroelectrics are disordered dipole-media in which nanosized dipoles ordered clusters are randomly distributed.^{10,11}

Nowadays it is believed that an adequate description of relaxors is given by microscopical models like the spherical random bond-random field model (SRBRF).¹² Other phenomenological model has been also proposed to study the response behavior of relaxors.¹³ However, these models do not include the coupling between polarization and deformation. Due to this, in this work, we use an older approach, which is based on the use of local properties, which vary along the sample. If these properties depend on a variable X characterizing the composition, local transitions take place at different conditions in nanoregions with differing local values of X .^{8,9,14} In particular, we assume the existence of local temperatures for the appearance of local polarization. We point out that this is a phenomenological approach, but we expect that it is adequate for our purpose. We do not study the frequency dependence of the relaxor parameters, due to restrictions of the model. Our goal is to consider some other aspects concerning ferroelectric relaxors that are still unclear. For instance, it is not well known if the parameters appearing in the S - P coupling have strong variation with disorder or temperature along the transition, or it can be considered almost constant.¹⁵ As a consequence, it has been proposed that the behaviour of the elastic constants along the relaxor ferroelectric phase transition could be explained assuming variations of the coupling. On the other hand, the role of the diffuseness in the dependence of the elastic constants with temperature is still not well understood. It is noteworthy that the coupling parameters are of great interest because they can be used to predict the piezoelectric behavior of these materials.

The aim of the present work is to develop a procedure that allows us to obtain the elastic constants in relaxors for temperatures around T_m . As already mentioned, we do not attempt to model the dependence of the relaxor parameters with the frequency. The values of these parameters depend on the frequency¹⁶ but this dependence is not explicitly described in the present theory.

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To obtain the values of the polarization, strain, and elastic constants, we minimize the free Landau-Devonshire energy.^{6,7,17} We compared the results of the present model with experimental data given in the literature of ultrasonic velocity in PLZT and $\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$ ceramics (PCT).

II. DESCRIPTION OF ELASTIC MODULUS VARIATION WITH TEMPERATURE

A. Landau-Devonshire theory

The study of the variations of the elastic constants in the ferroelectric transition can be done using a Landau free energy, which includes couplings between the polarization \mathbf{P} and the strain \mathbf{S} . The free energy can be expanded as

$$F(\mathbf{P}, \mathbf{S}) = aP^2 + bP^4 + kS^2 + F_c(\mathbf{P}, \mathbf{S}) + F_0, \quad (1)$$

where $a = a_0(T - T_c)$, being a_0 a constant, T_c is the Curie critical temperature, b, k are positive constants, and P and S are the magnitudes of \mathbf{P} and \mathbf{S} (the vector formed by the principal components of the strain). $F_c(\mathbf{P}, \mathbf{S})$ is the coupling term which contains the interaction between the polarization and the strain. It can be written as

$$F_c(\mathbf{P}, \mathbf{S}) = \sum_{ik} \beta_{ik} P_i S_k + \sum_{ikl} q_{ikl} P_i P_l S_k + \dots \quad (2)$$

We must comment that some terms in this series may be forbidden by symmetry. For instance, the bilinear terms $P_i S_k$ are forbidden in the cubic phase. However, their presence can be justified if there are departures from the strictly cubic symmetry. We will return to this point later.

From the expression of the free energy (1), the difference between polar (P) and non-polar (NP) elastic constants Δc can be obtained⁵

$$\Delta c = c_{mn}^P - c_{mn}^{NP} = \sum_{kl} \frac{\partial^2 F}{\partial S_m \partial P_k} \chi_{kl}^{-1} \frac{\partial^2 F}{\partial S_n \partial P_l}, \quad (3)$$

where χ_{kl} is the susceptibility and c_{mn} is the elastic constants. In order to simplify the expression (2), we will assume that the components of \mathbf{P} and \mathbf{S} do not refer to the same axes. The components of \mathbf{P} refer to a set of axes such that one of them coincides with the direction of \mathbf{P} . Thus, we shall have $P_1 = P, P_2 = P_3 = 0$. On the other hand, the components of \mathbf{S} refer to the principal axes of the strain tensor. We still can use (2), since it is a general Taylor expansion, which becomes

$$F_c(\mathbf{P}, \mathbf{S}) = F_c(P, \mathbf{S}) = \sum_k \beta_{1k} P S_k + q_{11k} P^2 S_k + \dots$$

We will assume that $\beta_{1k} = \beta/3, q_{11k} = q/3$ for all k . If we define $S = (\sum_k S_k)/3$ (the S_k 's may be different), we can write the above expression as

$$F_c(\mathbf{P}, \mathbf{S}) = \beta P S + q P^2 S + \dots \quad (4)$$

With these assumptions, using Eqs. (2) and (3), and retaining the first terms of the expansion (2), the difference Δc becomes

$$\Delta c = c^P - c^{NP} = -(\beta + qP)^2 \chi. \quad (5)$$

In the particular cases in which the S - P coupling has only the quadratic term in P ($\beta=0$), or only the linear term in P ($q=0$), the dependence of Δc have the forms shown in Figure 1.

It has been pointed out by Barret¹⁸ that the non polar term c^{NP} can be approximated by a linear function of temperature in KTaO_3 . If we assume this approximation holds, we can write

$$c^{NP} = c_0 + \alpha T. \quad (6)$$

Then, the elastic constants can be expressed as

$$c^P = -(\beta + qP)^2 \chi + c_0 + \alpha T.$$

The theoretical values of Δc can be obtained as a function of the parameters q, β , and T_c by means of the minimization of the free energy (1).

In the above description, it was assumed that the state is uniform along the sample. The relaxors, however, are highly inhomogeneous materials. As a consequence, the susceptibility does not have a sharp peak but instead presents a broad curve with a maximum at a temperature T_m . If the usual Landau-Devonshire theory is used, the temperature dependence of the elastic modulus that one obtains does not reproduce those observed experimentally in relaxors.¹⁷

In the literature, different phenomenological expressions to represent the susceptibility in relaxors, like those given in Refs. 4 and 19, have been proposed. In the present work, we shall obtain the susceptibility of the system through an average over nanoregions.

As we already mentioned, the term PS in the S - P interaction is in principle forbidden by symmetry in the cubic phase. However, there are deviations from the cubic symmetry when clusters are present. This situation occurs for temperatures above and below T_m , since the polar nanoregions begin to appear at a temperature $T_B > T_m$.⁹ For this reason, we allow the presence of this term.

B. Description of the relaxor state

As it has been already mentioned, we shall consider that the system is divided into clusters, each of them with their own critical temperature. We do not attempt to describe the

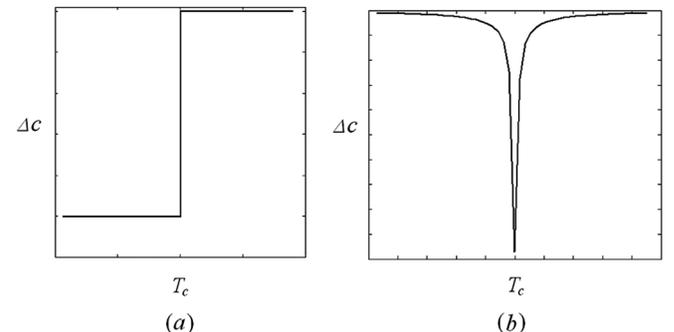


FIG. 1. Dependence of Δc with temperature for the cases in which (a) the coupling is nonlinear in P ($\beta=0$) and (b) the coupling is linear in P ($q=0$).

origin of the nanoregions. We shall assume that they are present (which is a widely accepted fact⁹) and introduce a statistical description for the Curie temperatures of the nanoregions. Then, we define the distribution function $W(\theta_l)$ for the critical temperatures of the clusters, such that $W(\theta_l)d\theta_l$ gives the fraction of nanoregions that have their critical temperatures between θ_l and $\theta_l + d\theta_l$.

We shall assume that the critical temperature θ_l of the cluster is only dependent on the cluster size v_l . A related simplification has been performed in Ref. 14, where it was assumed that the activation energy for fluctuations is proportional to the volume cluster. Thus, the average of a given quantity Q is obtained as

$$\bar{Q} = \frac{\int_{\theta_{\min}}^{\theta_{\max}} Q v_l(\theta_l) W(\theta_l) d\theta_l}{\int_{\theta_{\min}}^{\theta_{\max}} v_l(\theta_l) W(\theta_l) d\theta_l}. \quad (7)$$

Here, θ_{\min} y θ_{\max} are the maximum and minimal values that the critical temperatures can take. By defining $g(x) = v(x)W(x)$, we can write

$$\bar{Q} = \frac{1}{N} \int_{\theta_{\min}}^{\theta_{\max}} Q g(\theta_l) d\theta_l, \quad (8)$$

where

$$N = \int_{\theta_{\min}}^{\theta_{\max}} g(\theta_l) d\theta_l.$$

Since the Curie temperature varies along the sample, we define a local susceptibility $\chi_l(\theta_l)$, which relates the applied electric field and the polarization of the cluster. Since the clusters are small in comparison with the sample, we allow the susceptibility to have a different form than those of the susceptibility of a clean ferroelectric system. We shall describe the susceptibility of the nanoregions by the continuous function

$$\chi_l = \frac{\chi_{l0}}{\sqrt{1 + ((T - \theta_l)/d)^2}}. \quad (9)$$

We note that from this expression, we can recover the clean dependence $\chi = cte/(T - T_c)$ by taking the limit $d \rightarrow 0$. For finite d , this function is smooth with a broadening that is proportional to d . Using Eq. (8), we obtain the averaged quantities

$$\begin{aligned} \Delta c(T) &= \frac{1}{N} \int_{\theta_{\min}}^{\theta_{\max}} \Delta c_l(\theta_l, T) g(\theta_l) d\theta_l, \\ \chi(T) &= \frac{1}{N} \int_{\theta_{\min}}^{\theta_{\max}} \chi_l(\theta_l, T) g(\theta_l) d\theta_l. \end{aligned} \quad (10)$$

The values of $\Delta c_l(\theta_l, T)$ are obtained by the minimization of the free energy F_l for each cluster, given by

$$F_l(P_l, S_l) = a_l P_l^2 + b P_l^4 + k S_l^2 + \beta P_l S_l + q P_l^2 S_l,$$

where the first coefficient in the expansion is $a_l = a_0(T - \theta_l)$. We note that an equivalent procedure is to write an averaged free energy

$$F = \frac{1}{N} \int_{\theta_{\min}}^{\theta_{\max}} F_l(P_l, S_l, \theta_l) g(\theta_l) d\theta_l$$

and then to minimize it, obtaining the same results as (10). Concerning the function $g(\theta_l)$, we shall assume that this distribution has the Gaussian form

$$g(\theta_l) = A e^{-(\theta_l - T_m)^2/D^2},$$

where D and A are constants, and T_m is the temperature at which the averaged susceptibility is maximal. A relevant parameter of the model is the ratio $\xi = D/d$. This quantity will be taken as a free parameter, which shall be determined with the fittings of the curves. Other quantity of interest is $\Gamma = \Delta/T_m$, where Δ measures the broadening of the susceptibility. We define $\Delta = T_2 - T_1$, where T_2, T_1 are the temperatures at which $\chi = \chi(T_m)/2$, i.e., the susceptibility decays to half of its maximal value. Since Δ describes the broadening of the peak, Γ can be used as a measure of the diffuseness of the phase transition.^{3,9}

From now on, we adopt that $\theta_{\max, \min} = T_m \pm 2.3 D$. For these temperatures, the values of the Gaussian distribution $g(\theta)$ are very small, and integration outside the range $(\theta_{\max}, \theta_{\min})$ has a negligible contribution. In Figure 2, shapes of g , χ_l , and the total susceptibility χ , are shown for typical values of the parameters used in this work.

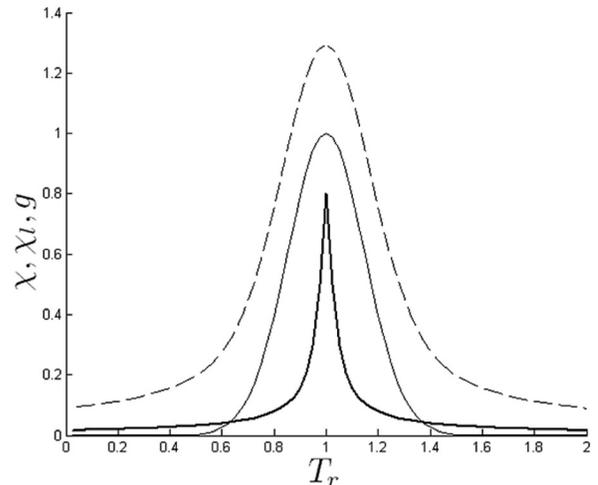


FIG. 2. Comparison of the curves for $\chi_l(T)$ (thick line), $g(T)$ (thin line) and $\chi(T)$ (dashed line), for $d/T_m = 0.02$, $\xi = 10$.

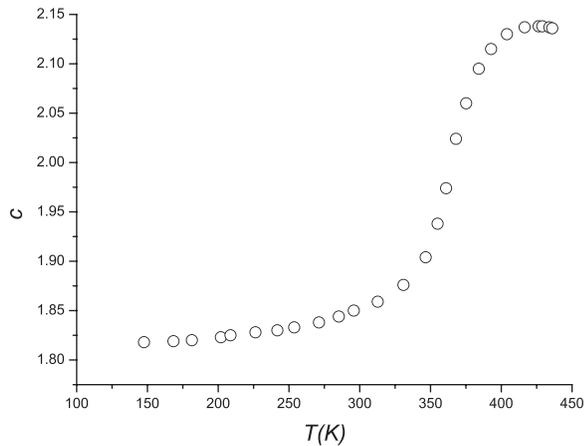


FIG. 3. Elastic constant for PCT 47.5 as a function of temperature, in units $\text{kg/ms}^2 \times 10^{11}$.

III. NUMERICAL RESULTS

The values of α and c_0 appearing in (6) were obtained directly from the experimental data by fitting the elastic constant to this linear expression at temperatures above T_m , for values of T for which it no polar contribution is expected. The values of Δc are thus obtained through the difference $\Delta c = c_p - (c_0 + \alpha T)$. The theoretical values of Δc were obtained as a function of q , β , and T_m by minimization of the free energy (1), and the optimized values of these parameters were determined by fitting the curves of Δc to the experimental values. We shall denote as T_m^* the value of T_m that is obtained from the fitting. We will also use the reduced temperature T_r defined as $T_r = T/T_m^*$.

A. Results with $(\text{Pb}_{1-x}\text{Ca}_x)\text{TiO}_3$

In this section, we compare theoretical and experimental results for the PCT ceramics. In Figure 3, the values of the elastic constant for the PCT 47.5 are shown.² When we extract the non polar component to calculate Δc , the results shown in Figure 4 are obtained. As it can be seen, the curve $\Delta c(T)$ takes a linear dependence at below T_m , but with a positive slope. This dependence cannot be reproduced with the

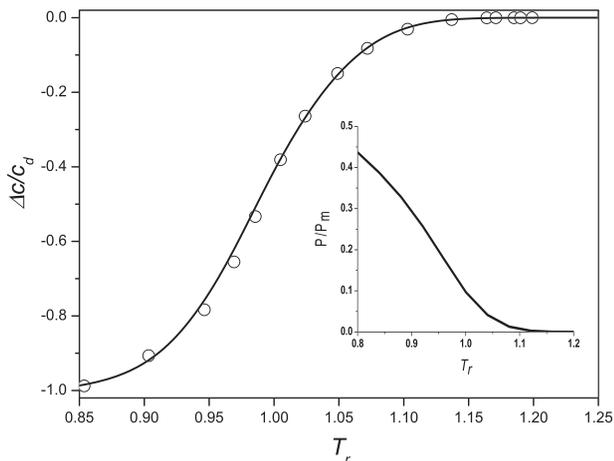


FIG. 4. Fitted curve for PCT 47.5 (5 MHz), where the used parameter values are $d/T_m^* = 0.008$, $q = 0.1$, $\beta = 0$; $\zeta = 10$, $T_m^* = 368$ K ($\Gamma = 0.18$). The inset shows the polarization.

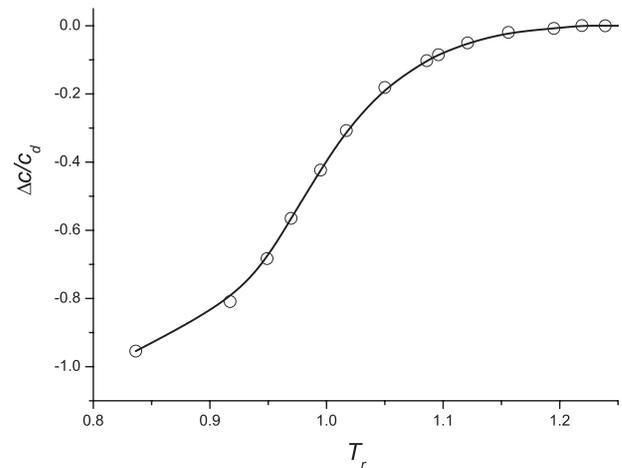


FIG. 5. Fitted curve for PCT 50 (5 MHz), corresponding to $d/T_m^* = 0.01$, $q = 0.1$, $\beta = 0$, $\zeta = 10$, $T_m^* = 335$ K ($\Gamma = 0.23$).

coupling of the form (3). This is probably because the theory presented here is not applicable for temperatures which are well below T_m , due to the presence of more complex phases with strong interaction between clusters.

The good results that were obtained with the fittings (Figures 4–7) show that the dependence of c with temperature can be reproduced with parameters couplings β , q that are independent of temperature.

In general, the best fittings were obtained with values of d which are small in comparison with D , ($d/D \sim 0.1$ or less). This means that the local susceptibilities are very sharp in comparison with the distribution of critical temperatures, and particularly in comparison of the total susceptibility of the system χ .

B. PLZT ferroelectric ceramics

In this section, we perform a comparison with measurements made on $(\text{Pb/La})(\text{Zr/Ti})\text{O}_3$ ferroelectric ceramics, reported by Silva *et al.*¹⁵ Figures 8 and 9 show the fittings of the theoretical curve with the experimental data corresponding to $(\text{Pb}_{0.95}\text{La}_{0.05})(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9875}\text{O}_3$ (PLZT 5/65/35) and $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.98}\text{O}_3$ (PLZT 8/65/35). In these

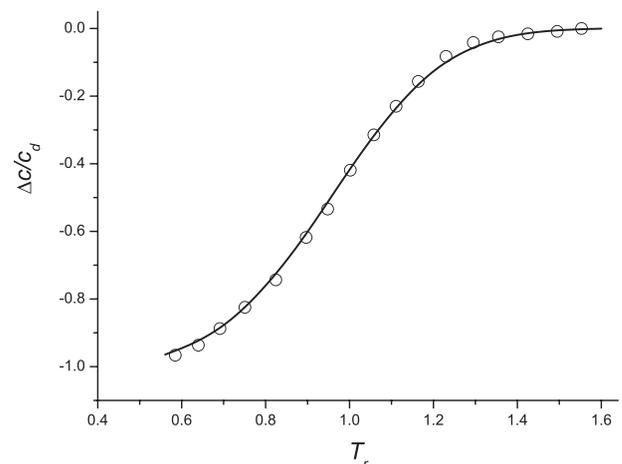


FIG. 6. Fitted curve for PCT 55 (5 MHz), corresponding to $d/T_m^* = 0.024$, $q = 0.1$, $\beta = 0$, $\zeta = 10$, $T_m^* = 247$ K ($\Gamma = 0.57$).

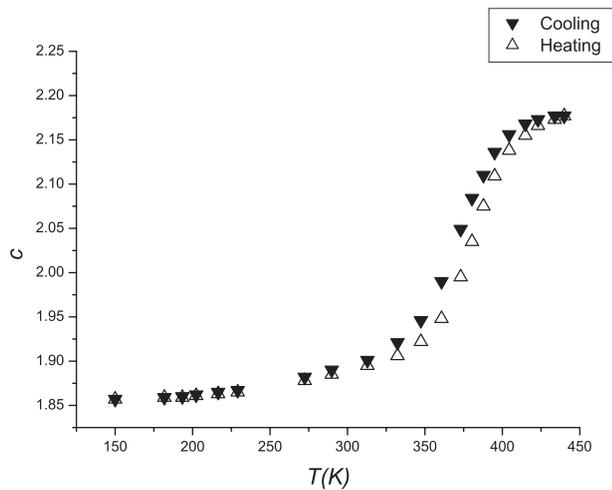


FIG. 7. Elastic constant for PCT 47.5 (at 10 MHz) showing the hysteresis in the cooling (triangles)-heating (circles) runs.

figures, the vertical axis corresponds to $\Delta c/c_d$, where c_d is the difference between the maximal and minimal values of Δc in the interval of temperatures considered. The fitted values of the parameters are indicated in the captions, and the variation of the polarization in PLZT 5/65/35 is shown in Figure 8.

The fit of velocity experimental data of (Pb/La)(Zr/Ti)O₃ ferroelectric ceramics, reported by Silva *et al.*, was realized with our model on the full temperature interval of the phase transition. As it can be seen, the strengths values for the linear and nonlinear couplings are almost the same for the two impurity concentrations. On the other hand, the notorious difference between the two samples is found in the value of Γ , i.e., the diffuseness of the transition. Thus, it is the change in the diffusiveness that produces the modification in the curve of $c(T)$.

At this point, we comment that the parameters of the model, q , β , T_m^* , and D , are expected to be frequency dependent. This is very clear in the case of T_m^* and D , since it is well known that T_m and the broadening of the susceptibility peak are frequency dependent in relaxors. However, we have not quantified the frequency dependence of q and β .

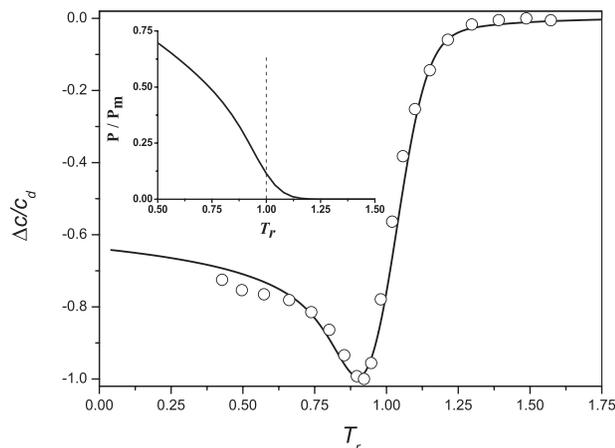


FIG. 8. Comparison between theoretical and experimental values for $\Delta c/c_d$ as a function of the reduced temperature T_r in PLZT 5/65/35. The used values of the parameters in this curve are $q=0.1$, $\beta=0.011$, $d=0.0125$; $\xi=10$, $\Gamma=0.4$. The polarization is shown in the inset.

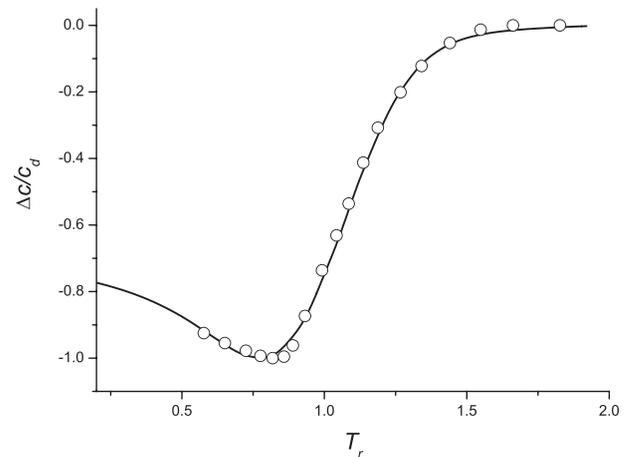


FIG. 9. Same as Figure 8 for PLZT 8/65/35, with $q=0.1$, $\beta=0.014$, $d=0.025$; $\xi=10$, $\Gamma=0.91$.

The theoretical description of these dependences is beyond the possibilities of the present model. In order to do this task, we must use other models (like those cited in the introduction) with which the dynamics of the relaxors can be reproduced.

IV. CONCLUSIONS

The temperature dependence of the elastic constants in relaxor ferroelectrics was studied with a composed Landau-Devonshire free energy having a coupling interaction between polarization and strain, which includes linear and quadratic terms in P .

With this procedure, we obtained very good fits of $c(T)$ in a temperature interval around T_m , and determinate the coupling P - S and the influence of the diffuseness on the $c(T)$ curves.

One important result obtained by us is that the coupling appears invariant at temperatures above and below T_m , in contrast with what is sometimes assumed. Also our results show that although diffuseness changes significantly with the doping level, the strengths of the couplings between polarization and strain remain almost unchanged. This fact was observed in both PCT and PLZT ceramics. This suggest that the shapes of $c(T)$ curves in these materials are also related with the diffuseness, instead of only being caused by changes in the S - P couplings. This shows that the diffuseness must be taken into account in the theoretical description of the elastic modulus in relaxors, in order to obtain accurate results.

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