

Piezoelectric softening in ferroelectrics: Ferroelectric versus antiferroelectric $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ F. Cordero,¹ F. Craciun,¹ F. Trequattrini,^{2,1} and C. Galassi³¹*CNR-ISC, Istituto dei Sistemi Complessi, Area della Ricerca di Roma–Tor Vergata, Via del Fosso del Cavaliere 100, I-00133 Roma, Italy*²*Dipartimento di Fisica, Università di Roma “La Sapienza,” Piazzale Aldo Moro 2, I-00185 Roma, Italy*³*CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Via Granarolo 64, I-48018 Faenza, Italy*

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The traditional derivation of the elastic anomalies associated with ferroelectric (FE) phase transitions in the framework of the Landau theory is combined with the piezoelectric constitutive relations instead of being explicitly carried out with a definite expression of the FE part of the free energy. In this manner it is shown that the softening within the FE phase is of electrostrictive and hence piezoelectric origin. Such a piezoelectric softening may be canceled by the better known piezoelectric stiffening, when the piezoelectric charges formed during the vibration are accompanied by the depolarization field, as for example in Brillouin scattering experiments. It is therefore possible to evaluate the average piezoelectric coupling from the usual elastic measurements of unpoled ceramics, where the piezoelectric stiffening does not occur. As experimental validation, we present new measurements on Zr-rich lead zirconate titanate (PZT), where the FE phase transforms into antiferroelectric on cooling or doping with La, and a comparison of existing measurements made on FE PZT with low frequency and Brillouin scattering experiments.

DOI: [10.1103/PhysRevB.93.174111](https://doi.org/10.1103/PhysRevB.93.174111)**I. INTRODUCTION**

The structural ferroelastic transitions are accompanied by elastic softening [1], and the same is true for most ferroelectric (FE) [2], magnetic, and electronic transitions whose order parameter is coupled to strain [3]. The softening starts in the high temperature phase when approaching the transition temperature, and can be directly or indirectly associated with a soft mode, or precursor fluctuations. In the low temperature phase, the elastic constants generally partially or completely restiffen, partly due to the freezing of the fluctuations, or even become much stiffer than in the high temperature phase, as in systems where a charge disproportionation and/or charge ordering transitions freezes the dynamic Jahn-Teller fluctuations [4]. The FE and antiferroelectric (AFE) transitions are also ferroelastic and therefore are accompanied by sizable softening, but the shape of the compliance curves versus temperature strongly depends on the material and also on the measurement frequency and technique. An additional extrinsic softening mechanism in the FE state, especially important at the lowest frequencies, is the motion of the domain walls [5,6].

We revisit the phenomenological theory of the classical ferroelectrics describable in terms of a Landau free energy with the polarization as primary order parameter and electrostrictive coupling to strain in the paraelectric (PE) phase, and neglecting other order parameters with possible formation of heterogeneous states. It is argued that, under these conditions, the main intrinsic contribution to the softening within the FE phase is of piezoelectric origin, but can be completely canceled by the so-called piezoelectric stiffening when the electric depolarization fields accompanying the piezoelectric charge can fully develop. As examples where these phenomena are particularly evident, we present new dielectric and elastic measurements on Zr-rich lead zirconate titanate (PZT), where the FE phase can be turned into AFE by cooling or doping with La, and compare existing low frequency [7] and Brillouin scattering [8] experiments on PZT at the morphotropic phase boundary between the rhombohedral and tetragonal FE phases.

II. EXPERIMENT AND RESULTS

Ceramic samples of $\text{Pb}_{1-3x/2}\text{La}_x\text{Zr}_{1-y}\text{Ti}_y\text{O}_3$ [PLZT $100x/100(1-y)/100y$] with $y = 0.046$ and $x = 0, 0.02$ were prepared by the mixed-oxide method in the same manner as a previous series of samples [9,10]. The oxide powders were calcined at 700°C for 4 h, pressed into bars, sintered at 1250°C for 2 h and packed with $\text{PbZrO}_3 + 5 \text{ wt } \% \text{ excess ZrO}_2$ to prevent PbO loss. The powder x-ray diffraction analysis did not reveal any trace of impurity phases. The densities were about 95% of the theoretical values and the grains were large, with sizes of $5\text{--}20 \mu\text{m}$. For the anelastic experiments samples were cut as thin bars 4 cm long and 0.6 mm thick, and electrodes were applied with Ag paint. The Young's modulus or its reciprocal, the compliance s , was measured by suspending the bar on two thin thermocouple wires and electrostatically exciting the flexural resonance [11]. The compliances are shown normalized to their values s_0 in the PE phase, in terms of the resonance frequency $f \sim 1 \text{ kHz}$: $s(T)/s_0 = [f_0/f(T)]^2$. The dielectric permittivity ϵ was measured on 0.7-mm-thick disks with diameters of 12 mm by means of a HP 4284A LCR meter with a four-wire probe and an electric field of 0.5 V/mm, between 0.2 and 200 kHz.

According to the phase diagram proposed by Asada and Koyama [12] for PLZT $x/95/5$, below T_C the La-free sample becomes rhombohedral (R) FE, while below T_{AF} it becomes orthorhombic (O) AFE, but for $x(\text{La}) > 0.01$ the intermediate phase is incommensurate (IC) AFE instead of R-FE, with reduced T_C and enhanced T_{AF} . In our samples the Zr/Ti ratio is very close to 95/5 and both the dielectric and elastic measurements conform to the phase diagram of Ref. [12]. Figure 1 presents the permittivity ϵ measured at 1 kHz and the normalized compliance s/s_0 measured at $\sim 1.7 \text{ kHz}$ during heating. Starting from high temperature, both permittivity curves show the Curie-Weiss rise up to T_C , followed by a drop due to the first order nature of the FE and IC-AFE transition, and an additional decrease below T_{AF} , where the susceptibility in a fully ordered AFE state is quite reduced with respect to a

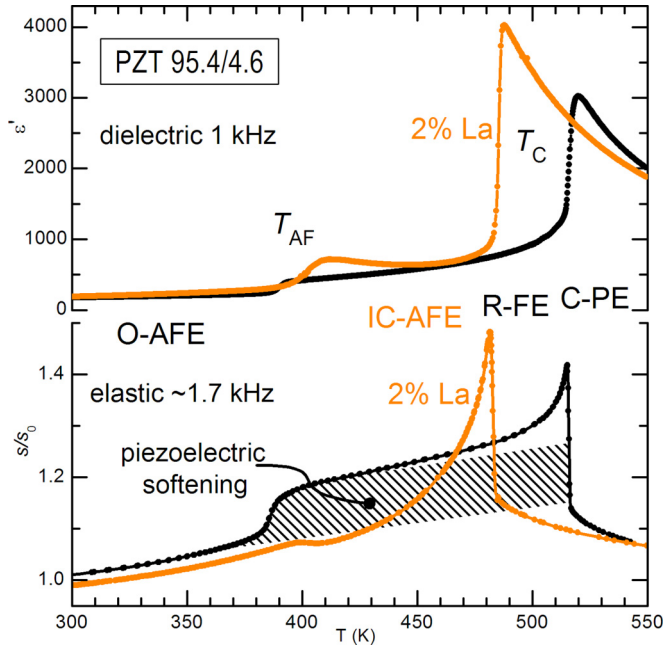


FIG. 1. Dielectric permittivity ϵ and compliance s of PLZT 100x/95.4/4.6 with $x = 0$ and 0.02 measured during heating. The ranges of the various phases are indicated. The dashed region is identifiable with the piezoelectric softening in the FE phase.

FE or IC state. While there is no qualitative difference between the ϵ curves of the sample with intermediate R-FE and IC-AFE phases, the difference is outstanding in the s curves: the FE phase has an additional roughly constant softening, indicated as a hatched area, completely missing in the IC-AFE phase, so that the step at T_{AF} is even inverted in sign.

III. DISCUSSION

The piezoelectric softening is not generally known with this name and is not always evident as such in the curves of the elastic compliance or modulus versus temperature. In fact, it may be masked by precursor and fluctuation effects near the transition, by the domain wall motion, or the occurrence of other transitions at lower temperature. The effect is instead evident in the pair of PLZT 100x/95.4/4.6 compositions in Fig. 1. In fact, apart from the precursor softening approaching T_C from the PE phase and the peaked contribution just below T_C , which is common to both compositions, a roughly constant softening, shaded in Fig. 1, is visible only within the FE phase of the La-free sample. The softening abruptly disappears when the R-FE phase transforms into O-AFE and never appears in the La-doped sample, where also the intermediate phase is AFE, instead of FE. The $s(T)$ curve of the undoped sample itself and even more so the comparison with $s(T)$ with La doping clearly indicate that a roughly temperature independent softening is associated with the FE state, indicated as a hatched region in Fig. 1.

According to the Landau theory of phase transitions, the standard treatment of the elastic anomaly at a FE transition [2] consists in establishing an expansion $G_0(\mathbf{P})$ of the free energy in powers of the polarization \mathbf{P} with enough terms to reproduce the features of the relevant region of the phase diagram. This

G_0 is inserted in place of $U - TS$ in the elastic Gibbs energy [13]

$$G_1 = U - TS - \sigma : \epsilon \quad (1)$$

so that

$$G_1 = G_0(\mathbf{P}) - \frac{1}{2} \sigma : \mathbf{s}^0 : \sigma - \sigma : \mathbf{Q} : \mathbf{P}, \quad (2)$$

where σ and ϵ with components σ_{ij} and ϵ_{ij} are the stress and strain tensors, \mathbf{s}^0 with components s_{ijkl}^0 is the bare compliance in the absence of polarization, hence often indicated as \mathbf{s}^D (superscript D meaning “at constant D ”), where $\mathbf{D} = \mathbf{P} + \epsilon \cdot \mathbf{E}$, \mathbf{Q} with components Q_{ijkl} is the electrostrictive coefficient, and $\mathbf{P}\mathbf{P}$ is a dyad with components $P_i P_j$; a single dot indicates scalar product (summation over repeated indices) over one index, while the semicolon indicates summation over a pair of indices. For full derivations see the Appendix. The differential of (1) is $dG_1 = -SdT - \epsilon : d\sigma + \mathbf{E} \cdot d\mathbf{D}$, so that the strain is $\epsilon = -\partial G_1 / \partial \sigma$. The compliance \mathbf{s} softened by the change of $\mathbf{P}(\sigma)$ under the application of the measuring stress is often called \mathbf{s}^E , being the one measured in the absence of an electric field, that also would change \mathbf{P} ; it can be calculated as

$$\begin{aligned} \mathbf{s}^E &= \frac{d\epsilon}{d\sigma} = \frac{d}{d\sigma} \left(-\frac{\partial G_1}{\partial \sigma} \right) = \frac{d}{d\sigma} (\mathbf{s}^0 : \sigma + \mathbf{Q} : \mathbf{P}\mathbf{P}) \\ &= \mathbf{s}^0 + 2\mathbf{Q} : \left(\mathbf{P} \frac{\partial \mathbf{P}}{\partial \sigma} \right). \end{aligned} \quad (3)$$

Usually the derivatives are explicitly calculated for specific expansions $G_0(\mathbf{P})$. In the simplest possible case

$$G_0(P) = \frac{a}{2} P^2 + \frac{b}{4} P^4 \quad (4)$$

with $a = \alpha(T - T_C)$, the temperature dependencies of the spontaneous polarizations and their stress derivatives cancel each other, and one obtains [2,14]

$$\mathbf{s}^E(T > T_C) = \mathbf{s}^0, \quad (5)$$

$$\mathbf{s}^E(T < T_C) = \mathbf{s}^0 + \frac{2\mathbf{Q}\mathbf{Q}}{b}, \quad (6)$$

namely, a steplike softening below T_C . Actually, $Q_\alpha Q_\beta$ might be negative for $s_{\alpha\beta}$ with $\alpha \neq \beta$ [$\alpha \equiv ij$ in Voigt notation [15] (see Appendix), and with a scalar order parameter $Q_{\alpha ij} \rightarrow Q_\alpha$], resulting in a stiffening, but this eventuality does not seem to be important in ferroelectric perovskites, where the major effects are in the $s_{\alpha\alpha}$ components. For expansions $G_0(P)$ including higher powers of \mathbf{P} and anisotropic terms the expression of the softening becomes far more complicated than Eq. (6), but for our purposes G_0 can be left general, and we will rather express $\partial \mathbf{P} / \partial \sigma$ in terms of the piezoelectric constitutive relations [13,16]

$$\epsilon = \mathbf{s}^E : \sigma + \mathbf{d}^+ \cdot \mathbf{E}, \quad (7)$$

$$\mathbf{D} = \mathbf{d} : \sigma + \epsilon^\sigma \cdot \mathbf{E}, \quad (8)$$

where ϵ^σ is the dielectric permittivity at constant stress and the cross indicates conjugate tensor or transpose matrix. From Eq. (8) with $E = 0$ we see that $\mathbf{P} = \mathbf{d} : \sigma$ is the piezoelectric charge and $\frac{\partial \mathbf{P}}{\partial \sigma} = \frac{\partial \mathbf{D}}{\partial \sigma} = \mathbf{d}$ is the piezoelectric

coefficient. Deriving the equilibrium condition $0 = \frac{\partial G_1}{\partial \mathbf{P}}$ with respect to σ we can also express \mathbf{Q} in terms of \mathbf{d} as (Ref. [16] and Appendix)

$$\mathbf{d} = \frac{\partial \mathbf{P}}{\partial \sigma} = 2\epsilon \cdot \mathbf{Q} \cdot \mathbf{P}, \quad (9)$$

which expresses the well-known fact that the piezoelectricity (d) is electrostriction (Q) biased by the spontaneous polarization, so that finally the piezoelectric softening in Eq. (3) can be written as

$$\Delta \mathbf{s}^{\text{soft}} = \mathbf{s}^E - \mathbf{s}^0 = 4(\mathbf{Q} \cdot \mathbf{P}) \cdot \epsilon \cdot (\mathbf{Q} \cdot \mathbf{P}) = \mathbf{d}^+ \cdot \epsilon^{-1} \cdot \mathbf{d}. \quad (10)$$

Expressions equivalent to Eq. (10) have been used to describe the elastic response of deformation modes that are piezoelectric also in the PE phase, like the elastic constant c_{66} in potassium dihydrogen phosphate [17,18], but this formulation is general and clearly shows that, independently of the complications of the FE transformation, the origin of the additional softening in the FE phase is electrostrictive or equivalently piezoelectric. In a simple case like Eq. (4) it is $P^2 \propto \epsilon^{-1} \propto T$, so that their temperature dependencies cancel out and one remains with a constant softening in the FE phase, as in (6), but in general some temperature dependence can be expected, besides the fluctuation effects. Therefore, the piezoelectric contribution hatched in Fig. 1 is constant, but might well exhibit some enhancement on approaching T_C .

Notice also that from the magnitude of the piezoelectric softening of an unpoled ceramic material one does not obtain the same effective piezoelectric constants d_{33}^* , d_{31}^* , etc., as from a piezoelectrically excited poled sample, but an angular average of \mathbf{d} .

The \mathbf{s}^E compliance is measured when neither an external nor an internal depolarizing field \mathbf{E}^{dep} affects or neutralizes the piezoelectric strain. This is certainly the situation of resonant and subresonant measurements of unpoled ceramic samples, where the direction of the spontaneous \mathbf{P}_0 and the associated depolarization field changes randomly many times within the regions where \mathbf{P} accumulates the piezoelectric charges (electrodes and vibration nodes) and averages to zero. In the same situation is a poled crystal or ceramic whose electrodes are shorted or driven by a circuit with sufficiently low impedance. In these cases the complete piezoelectric softening, Eq. (10), is observed (see, e.g., the coincidence of the piezoelectric softening measured in (Ba,Ca)(Ti,Zr)O₃ with a dynamic mechanical analyzer, electrostatically excited free flexural resonance, and piezoresonance [19]), but otherwise the well-known phenomenon of piezoelectric stiffening [17,20–26] occurs, which we show now can exactly cancel the piezoelectric softening, leaving the bare elastic constant.

In the absence of mechanisms for neutralizing the piezoelectric charges $\delta \mathbf{P} = \mathbf{d} : \sigma$ (e.g., vibration of a poled sample with open electrodes), we are in the condition of constant $\mathbf{D} = \epsilon \cdot \mathbf{E} + \mathbf{P}$, where a change in $\delta \mathbf{P}$ causes a depolarization field $\delta \mathbf{E}^{\text{dep}} = -\delta \mathbf{P}/\epsilon$ that, according to the additional constitutive relationships [13,16]

$$\varepsilon = \mathbf{s}^D : \sigma + \mathbf{g}^+ \cdot \mathbf{D}, \quad (11)$$

$$\mathbf{E} = -\mathbf{g} : \sigma + \epsilon^{-1} \cdot \mathbf{D} \quad (12)$$

can be written as $\mathbf{E}^{\text{dep}} = -\mathbf{g} : \sigma$, and since $\mathbf{g} = \epsilon^{-1} \cdot \mathbf{d}$ (see Appendix),

$$\mathbf{E}^{\text{dep}} = -\epsilon^{-1} \cdot \mathbf{d} : \sigma. \quad (13)$$

This field causes an opposing stress with respect to the constant E condition, and its effect can be written with Eq. (7) as

$$\varepsilon = \mathbf{s}^E : \sigma - \mathbf{d}^+ \cdot \epsilon^{-1} \cdot \mathbf{d} : \sigma = \mathbf{s}^D : \sigma \quad (14)$$

in terms of a reduced and hence restiffened compliance \mathbf{s}^D . Therefore the relationship between compliance at constant E and D is

$$\Delta \mathbf{s}^{\text{stiff}} = \mathbf{s}^D - \mathbf{s}^E = -\mathbf{d}^+ \cdot \epsilon^{-1} \cdot \mathbf{d} = -\Delta \mathbf{s}^{\text{soft}}, \quad (15)$$

the piezoelectric stiffening simply cancels the piezoelectric softening and one remains with the compliance of the PE phase $\mathbf{s}^0 \equiv \mathbf{s}^D$.

Piezoelectric stiffening is known to occur in resonating devices [25] and to affect the propagation of elastic waves [21–24,26]. Moreover, if the material is conducting, the free charge may partially neutralize the depolarization fields and yield a dispersion in frequency of the relaxation type, with intermediate elastic constant between the completely softened or restiffened values [21].

In the case of the propagation of acoustic waves, the piezoelectric stiffening fully acts in a polarized material or even in unpoled ceramics if the wavelength is smaller than the size of the FE domains, as for Brillouin scattering. In both cases the depolarization field fully develops within each half wavelength within domains of uniform polarization. In this context the piezoelectrically softened elastic constant $\mathbf{c}^E = (\mathbf{s}^E)^{-1}$ is considered the reference, and expressions are provided for the restiffened constants $\mathbf{c}^D = \mathbf{c}^E + \Delta \mathbf{c}^{\text{stiff}}$ felt by a plane wave propagating along the direction $\hat{\mathbf{n}}$ [22–24,26]:

$$\Delta \mathbf{c}^{\text{stiff}}(\hat{\mathbf{n}}) = \frac{(\mathbf{e} \cdot \hat{\mathbf{n}})(\mathbf{e} \cdot \hat{\mathbf{n}})}{\hat{\mathbf{n}} \cdot \epsilon \cdot \hat{\mathbf{n}}}, \quad (16)$$

where the relationship between piezoelectric stress and strain coefficients is $\mathbf{e} = \mathbf{d} : \mathbf{c}^E$ (see Appendix). This formula can be rewritten in a manner directly comparable to Eq. (15); for special directions where only one of the tensor components projected onto $\hat{\mathbf{n}}$ is relevant,

$$\frac{\Delta c^{\text{stiff}}}{c^E} = \frac{(dc^E)^2}{c^E \epsilon} = \frac{d^2}{s^E \epsilon} = \frac{-\Delta s^{\text{soft}}}{s^E}. \quad (17)$$

Also for propagating acoustic waves, the piezoelectric softening may be canceled by the formation of the depolarization field.

Figure 2 presents an example where the clear piezoelectric softening measured at low frequency on a ceramic PZT sample is totally absent in the Brillouin scattering experiment. At the PZT 55/45 composition one crosses at T_{MPB} the morphotropic phase boundary (MPB) between R and tetragonal (T) FE phases, and further below T_T the oxygen octahedra undergo long-range tilting about the polar axis, which is a nonpolar mode. Accordingly, the compliance measured at ~ 1 kHz [7] with the same method as described here has a large jump below T_C , where the hatched region is considered piezoelectric softening, and is followed by a peak at T_{MPB} . As discussed elsewhere [9,14,27], this peak is due to an enhancement of

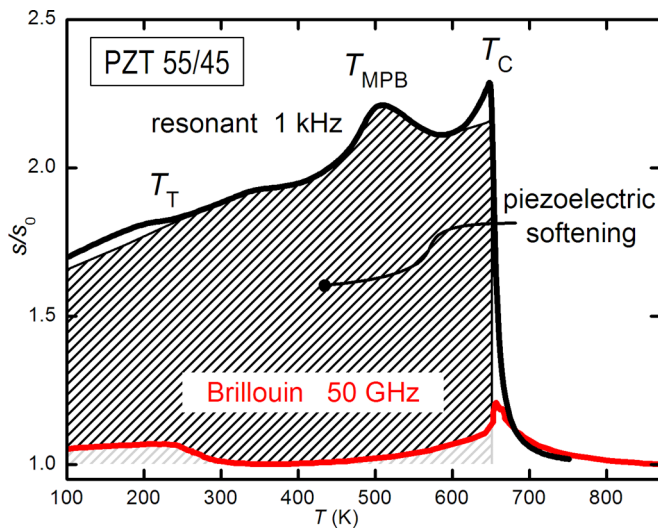


FIG. 2. Normalized compliance of PZT 55/45 measured with flexural resonance [7] at 1 kHz and Brillouin scattering [8] at 50 GHz.

the shear compliance Δs_{55} , which is approximately linearly coupled to the rotation of the polarization between the T [001] and the R [111] axis. Since this Δs_{55} is directly related to the FE state, it contributes to the piezoelectric coupling [27] and is totally considered piezoelectric softening. Instead, the step below T_T is not considered piezoelectric softening, because it is due to the antiferrodistortive octahedral tilting, which does not directly contribute to the polarization state. The lower curve in Fig. 2 is extracted as $s/s_0 = (\nu_0/\nu_B)^2$ from the Brillouin frequency shift $\nu_B \sim 50$ GHz for the LA mode along [100], as measured by Kojima *et al.* [8]. In this geometry the c_{11} constant is probed, which is responsible for the jump below T_C in the previous measurement, but the probed acoustic waves develop a longitudinal piezoelectric polarization that is completely canceled by the depolarization field and consequent piezoelectric stiffening, as in Eq. (17). Therefore, the piezoelectric softening is totally absent, including the enhancement at T_{MPB} related to s_{55} . On the other hand, the peaked softening due to the short-range polar fluctuations near T_C is clearly visible, because their correlation lengths are shorter than the Brillouin wavelength and there is no coherent depolarization field within a half wavelength. Also the step below T_T is fully visible, because it does not involve piezoelectricity.

The smallness of the softening in the Brillouin experiments compared to those at lower frequency has been noticed also for other FE materials, and explained in terms of dynamic response of the order parameter and domain wall motion [28], but besides relaxation and adiabatic versus isothermal effects, the piezoelectric stiffening from the depolarization field should also be taken into account.

It is interesting to compare the behavior of classic ferroelectrics such as PZT and BaTiO_3 , having a stable piezoelectric response in the FE phase, with the relaxor $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$, whose elastic constants have been measured by resonant ultrasound spectroscopy, with the option of detecting the signal also through the piezoelectric response of the sample itself [29]. In this manner it was possible to measure an

averaged piezoelectric response, which was sharply peaked at the transition temperature, but vanished at low temperature, in the absence of a strong electric field forcing the FE state out of a heterogeneous relaxor phase. Accordingly, also the elastic constants exhibited a sharp negative peak at nearly the same temperature, without evident residual piezoelectric softening at lower temperature.

IV. CONCLUSION

It is shown that, regardless of the possibly complicated phase diagram, within a FE phase the elastic constants undergo a softening due to the additional piezoelectric strain under the application of the probing stress. Such a strain can be reduced or canceled by the development of the depolarization field \mathbf{E}^{dep} due to the piezoelectric charges, through the well-known mechanism of the piezoelectric stiffening, which therefore restores the bare elastic constants of the paraelectric phase. The full piezoelectric softening can be observed in resonant and subresonant measurements of unpoled ceramic samples, where no coherent macroscopic \mathbf{E}^{dep} can develop, or also of poled samples where \mathbf{E}^{dep} is shorted by an external circuit. Instead, in Brillouin scattering experiments, where the wavelength of the probed acoustic waves is smaller than the domain size, a coherent \mathbf{E}^{dep} forms within each half wavelength and cancels the piezoelectric softening. It follows that the compliance curves versus temperature of unpoled ceramic samples indirectly probe the piezoelectric coupling, and for example allow one to distinguish FE from AFE phases and to identify temperature and composition regions of particularly high piezoelectricity.

Two experimental verifications are presented. Elasticity and dielectric measurements are carried out in PZT compositions where the FE phase turns into AFE by cooling or doping with La, with concomitant restiffening. In addition, for PZT 55/45 a comparison of the fully piezoelectrically softened Young's modulus with the unsoftened c_{11} elastic constant from the Brillouin scattering experiments of Kojima and co-workers is discussed [8].

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APPENDIX

The various equations used in the text are written out in terms of their components. Indices in Latin letters are the Cartesian components $i = 1-3$ of the electrical quantities, while the Greek letters are the stress/strain components in Voigt or matrix notation [15]: $ij = 11, 22, 33 \rightarrow \alpha = 1, 2, 3$, $ij = 12, 21 \rightarrow \alpha = 6$, $ij = 23, 32 \rightarrow \alpha = 4$, $ij = 13, 31 \rightarrow \alpha = 5$, with the additional rule that the components of ε , \mathbf{s} , and \mathbf{Q} have to be multiplied by 2 for each index $\alpha \geq 4$. The convention is adopted of summation over repeated indices, e.g., $\sigma_\alpha Q_{\alpha ij} P_i P_j \equiv \sum_{\alpha=1}^6 \sum_{i=1}^3 \sum_{j=1}^3 \sigma_\alpha Q_{\alpha ij} P_i P_j$.

1. Piezoelectric constitutive relations

The piezoelectric constitutive relations [Eqs. (7), (8) and (11), (12)] are [13,16]

$$\varepsilon_\alpha = s_{\alpha\beta}^E \sigma_\beta + d_{j\alpha} E_j, \quad (\text{A1})$$

$$D_i = d_{i\beta} \sigma_\beta + \epsilon_{ij}^\sigma E_j, \quad (\text{A2})$$

where $d_{j\alpha} = d_{\alpha j}^+$ and

$$\varepsilon_\alpha = s_{\alpha\beta}^D \sigma_\beta + g_{j\alpha} D_j, \quad (\text{A3})$$

$$E_i = -g_{i\beta} \sigma_\beta + \beta_{ij}^\sigma D_j, \quad (\text{A4})$$

$$\text{with } \beta_{ik} \epsilon_{kj} = \delta_{ij}. \quad (\text{A5})$$

The relationship between the piezoelectric constants \mathbf{d} and \mathbf{g} can be found as

$$g_{i\alpha} = \left(\frac{\partial \varepsilon_\alpha}{\partial D_i} \right)_\sigma = \left(\frac{\partial \varepsilon_\alpha}{\partial E_j} \frac{\partial E_j}{\partial D_i} \right)_\sigma \quad (\text{A6})$$

$$= d_{j\alpha} \beta_{ij}^\sigma = (\epsilon^{-1})_{ij}^\sigma d_{j\alpha}. \quad (\text{A7})$$

When dealing with the piezoelectric stiffening of the elastic constant $\mathbf{c} = \mathbf{s}^{-1}$, one makes use of another pair of constitutive relations [16]

$$\sigma_\alpha = c_{\alpha\beta}^E \varepsilon_\beta - e_{j\alpha} E_j, \quad (\text{A8})$$

$$D_i = e_{i\beta} \varepsilon_\beta + \epsilon_{ij} E_j, \quad (\text{A9})$$

and the relationship between the piezoelectric coefficients \mathbf{e} and \mathbf{d} is

$$e_{i\alpha} = \left(\frac{\partial D_i}{\partial \varepsilon_\alpha} \right)_E = \left(\frac{\partial D_i}{\partial \sigma_\beta} \right)_E \left(\frac{\partial \sigma_\beta}{\partial \varepsilon_\alpha} \right)_E = d_{i\beta} c_{\alpha\beta}^E. \quad (\text{A10})$$

2. Compliance in the absence of depolarization field

The differential of the internal energy is [13]

$$dU = TdS + \sigma_j d\varepsilon_j + E_j dD_j \quad (\text{A11})$$

with S = entropy, and ε and \mathbf{D} as independent variables. Since we need as independent variables T and σ , we use the elastic Gibbs energy

$$G_1 = U - TS - \sigma_\alpha \varepsilon_\alpha \quad (\text{A12})$$

whose differential is

$$dG_1 = -SdT - \varepsilon_\alpha d\sigma_\alpha + E_j dD_j. \quad (\text{A13})$$

In the absence of external fields one can deduce the phase transitions and phase diagram of the material by a suitable $G = U - TS$, which, applying the Landau theory of phase transitions to a ferroelectric, is expanded in powers of \mathbf{P} as $G_0(P)$. Of the additional terms of the expansion of the free energy in powers of the variables P , T , and σ we explicitly take into account only the elastic ($\propto \sigma_\alpha \sigma_\beta$) and electrostrictive ($\propto \sigma_\alpha P_i P_j$), since the piezoelectric ($\propto \sigma_\alpha P_i$) is generally absent in the paraelectric phases:

$$G_1 = G_0(P) - \frac{1}{2} \sigma_\alpha s_{\alpha\beta}^0 \sigma_\beta - \sigma_\alpha Q_{\alpha ij} P_i P_j, \quad (\text{A14})$$

where \mathbf{s}^0 is the bare elastic compliance in the absence of electrostrictive and hence piezoelectric effect. The compliance that is measured when \mathbf{P} can freely reach equilibrium with stress in the absence of external field is

$$s_{\alpha\beta}^E = \frac{d\varepsilon_\alpha}{d\sigma_\beta}, \quad (\text{A15})$$

where the strain can be deduced from Eqs. (A13) and (A14),

$$\varepsilon_\alpha = -\frac{\partial G_1}{\partial \sigma_\alpha} = s_{\alpha\beta}^0 \sigma_\beta + Q_{\alpha ij} P_i P_j, \quad (\text{A16})$$

where $\mathbf{Q} : \mathbf{PP}$ is the electrostrictive strain, which in the FE phase with $\mathbf{P} = \mathbf{P}_0 \neq 0$ becomes a piezoelectric strain. The compliance at constant \mathbf{E} , with \mathbf{P} and \mathbf{D} in equilibrium with the applied stress is

$$s_{\alpha\beta}^E = \frac{d\varepsilon_\alpha}{d\sigma_\beta} = s_{\alpha\beta}^0 + 2Q_{\alpha ij} P_i \frac{\partial P_j}{\partial \sigma_\beta}. \quad (\text{A17})$$

If $E = 0$, we can deduce from Eq. (A2)

$$\frac{\partial P_i}{\partial \sigma_\alpha} = \frac{\partial D_i}{\partial \sigma_\alpha} = d_{i\alpha} \quad (\text{A18})$$

and can express \mathbf{Q} in terms of \mathbf{d} . In fact, let us write the condition for the equilibrium (spontaneous) polarization

$$0 = \frac{\partial G_0}{\partial P_i} - 2\sigma_\beta Q_{\beta ij} P_j \quad (\text{A19})$$

and further derive with respect to σ_α , taking into account that G_0 depends on σ through \mathbf{P} and taking the limit $\sigma \rightarrow 0$,

$$\begin{aligned} 0 &= \frac{d}{d\sigma_\alpha} \left(\frac{\partial G_0}{\partial P_i} - 2\sigma_\beta Q_{\beta ij} P_j \right) \\ &= \frac{\partial^2 G_0}{\partial P_i \partial P_j} \frac{\partial P_j}{\partial \sigma_\alpha} - 2Q_{\alpha ij} P_j - O(\sigma), \end{aligned}$$

where the dielectric stiffness is

$$\frac{\partial^2 G_0}{\partial P_i \partial P_j} = \beta_{ij} = (\epsilon^{-1})_{ij} \quad (\text{A20})$$

and multiplying by ϵ and using (A18)

$$\frac{\partial P_i}{\partial \sigma_\alpha} = 2\epsilon_{ik} Q_{\alpha kl} P_l = d_{i\alpha} \quad (\text{A21})$$

so that finally the piezoelectric softening can be written as

$$\begin{aligned} \Delta s_{\alpha\beta}^{\text{soft}} &= s_{\alpha\beta}^E - s_{\alpha\beta}^0 = 2Q_{\alpha ij} P_i \frac{\partial P_j}{\partial \sigma_\beta} \\ &= 2Q_{\alpha ij} P_i 2\epsilon_{jk} Q_{\beta kl} P_l, \end{aligned} \quad (\text{A22})$$

and exploiting the symmetry $Q_{\alpha ij} = Q_{\alpha ji}$ we obtain the first part of Eq. (10),

$$\Delta s_{\alpha\beta}^{\text{soft}} = 4Q_{\alpha ji} P_i \epsilon_{jk} Q_{\beta kl} P_l \quad (\text{A23})$$

which can be further expressed in terms of the piezoelectric coupling \mathbf{d} using (A21) and inserting $\epsilon = \epsilon \cdot \epsilon^{-1} \cdot \epsilon$ or $\epsilon_{jk} = \epsilon_{jm} (\epsilon^{-1})_{mn} \epsilon_{nk}$ with $\epsilon_{jm} = \epsilon_{mj}$ and $d_{m\alpha} = d_{\alpha m}^+$,

$$\begin{aligned} \Delta s_{\alpha\beta}^{\text{soft}} &= 2\epsilon_{mj} Q_{\alpha ji} P_i (\epsilon^{-1})_{mn} 2\epsilon_{nk} Q_{\beta kl} P_l \\ &= d_{\alpha m}^+ (\epsilon^{-1})_{mn} d_{n\beta}, \end{aligned} \quad (\text{A24})$$

which is the last part of Eq. (10).

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