

Modeling of High-Signal Electrostriction. I

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A thermodynamical calculation of high-signal electrostriction, especially of ferroelectric materials, is proposed. It permits to model the high-signal electrostriction of the paraelectric and the fundamental switching behaviour of the ferroelectric phase. Extraordinary high-signal deformation curves can be explained, the influence of the thermodynamical coefficients can be estimated and the order of phase transitions can be determined experimentally from the high-signal deformation curves.

Key words: Electromechanical properties, Electrostriction, Ferroelectrics, Thermodynamic, Phase transition.

1. Introduction

In the last years a considerable number of publications has been dedicated to the electrostriction in several ferroelectric materials, especially in relaxor type ferroelectrics which exhibit anomalous large high-signal electrostrictive deformations (see e.g. [1–11]). Such investigations are stimulated by a continuously increasing interest in displacement transducers and the arising possibility to fabricate electrostrictive actuators.

The electrostriction is a quadratic electromechanical coupling mechanism. The corresponding equation reads

$$S_n = Q_{mn} P_m^2, \quad (1)$$

where S_n , Q_{mn} and P_m are the deformation, the electrostrictive coefficient relating to the polarization and the polarization, respectively.

Usually, the polarization P_m and hence the electrostrictive deformation is very small and can be referred to the electric field (E_m) as follows:

$$S_n = Q_{mn} \epsilon_{mm}^2 E_m^2 = R_{mn} E_m^2, \quad (2)$$

where ϵ_{mm} and R_{mn} are the dielectric permittivity and the electrostrictive coefficient relating to the field, respectively.

As long as ϵ_{mm} is small and field independent, (2) is valid within the whole field range and characterized by a constant R -coefficient. The observed deformations remain small. If, however, due to a higher per-

mittivity larger strain values are reached, such a simple relationship between strain and electric field is no longer useful. Since a higher permittivity is usually accompanied by an obvious field dependence of ϵ_{mm} , the typical high-signal deformation curve – observed e.g. in relaxor ferroelectrics – corresponds to a dependence presented in Figure 1.

In spite of the increasing interest in the application of electrostriction, relevant literature on the theoretical description of high-signal electrostriction is rather rare. On the other hand, such a theoretical description seems to be indispensable as the following results illustrate. The investigation of two different ferroelectric materials – $\text{Ba}(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ (BTS-10) and $0.55\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 + 0.45\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PMN-PSN) ceramics – has shown that a comparison of the weak-signal electrostrictive coefficients (determined at small deformation values) does not allow any prediction of the high-signal deformation (Figure 2).

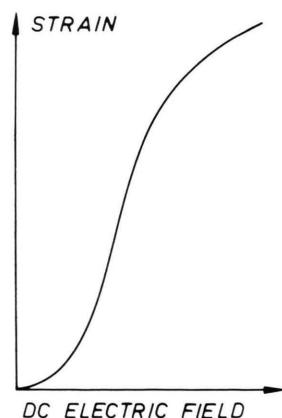


Fig. 1. Typical high-signal deformation curve of a relaxor ferroelectric.

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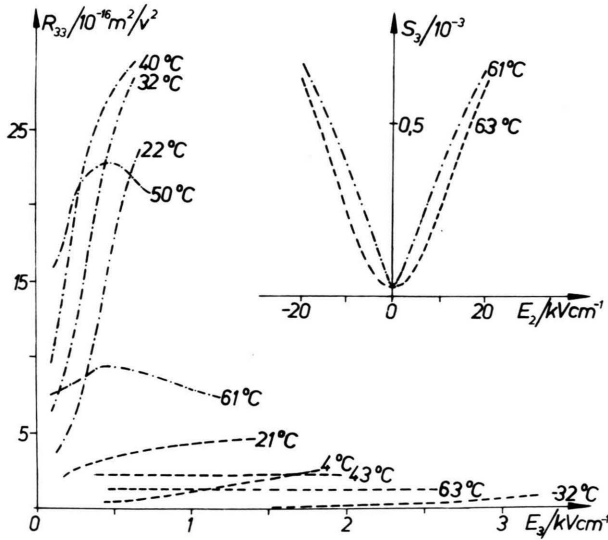


Fig. 2. Weak-signal electrostrictive R_{33} -coefficients of PMN-PSN (broken lines) and BTS-10 (dash-dotted lines) at different temperatures and the corresponding high-signal electrostriction near 60 °C.

Although the weak-signal R_{33} -coefficients differ considerably, the corresponding high-signal electrostriction (field dependence of the strain up to 20 kV/cm) is, due to qualitative differences in the field dependence of the strain, nearly the same (compare the curves at temperatures near 60 °C).

In Fig. 3 it can be seen what extraordinary shapes of the electrostrictive strain-field curves are possible. An efficient theoretical description of the high-signal strain-field dependence has to consider not only all potential cases but should also offer the possibility to predict the high-signal dependence even in a very high field range ($> 100 \text{ kV/cm}$). The latter can be of interest when very thin multilayer stacks are considered.

2. Basic Considerations

A first theoretical description was attempted by Smolensky et al. [6]. They proposed to discuss the high-signal deformation in terms of a power expansion of E . The disadvantage, however, is the missing validity at higher field values. Moreover, it is not possible to describe an occurring hysteresis or to determine the used expansion coefficients by thermodynamical methods.

Starting from the universal validity of (1) an alternative possibility on a thermodynamical basis can be

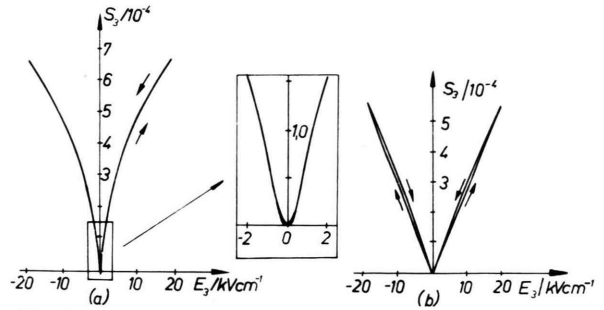


Fig. 3. High-signal electrostrictive deformation of $\text{Ba}(\text{Ti}_{0.8}\text{Sn}_{0.13})\text{O}_3$ at room temperature (a) and $\text{Ba}(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ at 60 °C (b).

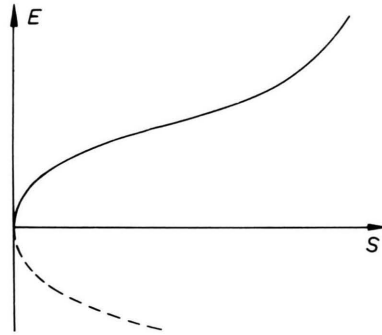


Fig. 4. The inverse function $E(S)$.

found. For that purpose we consider the Gibb's function of a uniaxial ferroelectric:

$$G_1 = G_{10} + \frac{(T - T_c)}{2 \varepsilon_0 C} P^2 + \frac{\xi}{4} P^4 + \frac{\zeta}{6} P^6. \quad (3)$$

From (1) follows

$$E(P) = \frac{\partial G_1}{\partial P} = \frac{(T - T_c)}{\varepsilon_0 C} P + \xi P^3 + \zeta P^5. \quad (4)$$

To obtain, however, an analytical expression $S(E)$ on the basis of (1), the inverse relationship $P(E)$ would be necessary. Since this is not trivial, let us look for an alternative. This can be the analytical calculation of the inverse function $E(S)$, which is illustrated in Figure 4. Of course it is without any physical sense, but it offers the possibility to describe the whole curve in an analytical way. It exhibits (excepting $S=0$) two solutions and can be obtained after the substitution of the inversion of (1),

$$P = \pm \sqrt{S/Q}, \quad (5)$$

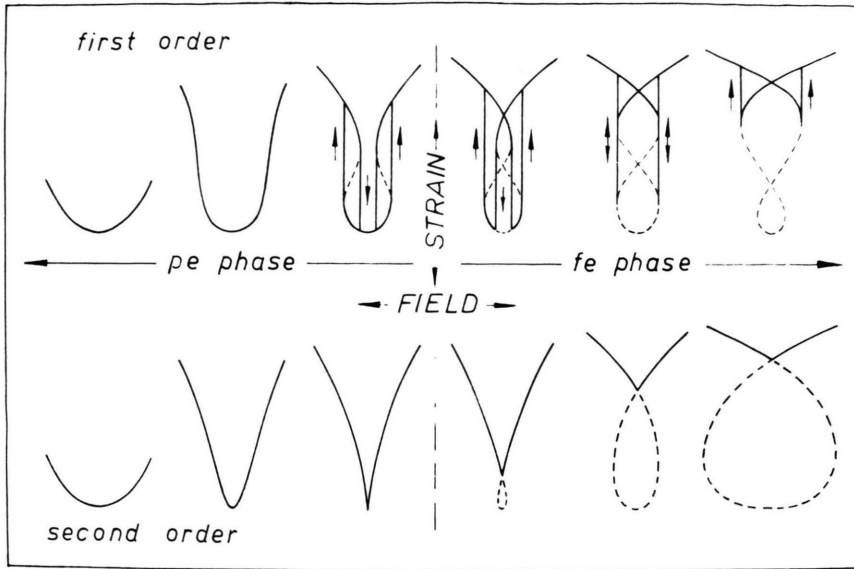


Fig. 5. Scheme of the evolution of the high-signal strain-field dependence resulting from (7) (for the explanation see text).

into (4)

$$E(S) = \pm \frac{(T - T_c)}{\varepsilon_0 C} \sqrt{S/Q} \pm \xi \sqrt{S^3/Q^3} \pm \zeta \sqrt{S^5/Q^5}. \quad (6)$$

An easy transformation yields the relation

$$E(S) = \pm \sqrt{\alpha S + \beta S^2 + \gamma S^3 + \mu S^4 + \nu S^5}, \quad (7)$$

where the coefficients α , β etc. are exclusively determined by the thermodynamical coefficients C , ξ , and ζ as well as by the electrostrictive coefficients Q , the Curie-temperature T_c and the temperature T . The corresponding equations read

$$\alpha = \frac{(T - T_c)^2}{QC^2 \varepsilon_0^2}, \quad (8)$$

$$\beta = \frac{2(T - T_c) \xi}{Q^2 C \varepsilon_0}, \quad (9)$$

$$\gamma = \frac{\xi^2 \varepsilon_0 C + 2(T - T_c) \zeta}{Q^3 C \varepsilon_0}, \quad (10)$$

$$\mu = \frac{2 \xi \zeta}{Q^4}, \quad (11)$$

$$\nu = \frac{\zeta^2}{Q^5}. \quad (12)$$

If the maximum deformation S is very small, (7) can be reduced to

$$E(S) = \pm \sqrt{\alpha S}, \quad (13)$$

Table 1. Characteristics of the coefficients α , β , γ , μ , and ν divided into the two types of phase transitions.

| | First order | Second order |
|----------|-----------------------------------------------------------|--------------------------|
| α | > 0 | > 0 |
| β | ≤ 0 if $T \geq T_c$ | ≥ 0 if $T \geq T_c$ |
| γ | ≥ 0 if $T \geq T_c - (\xi^2 \varepsilon_0 C)/2\zeta$ | $\xi^2/Q^3 > 0$ |
| μ | < 0 | $= 0$ |
| ν | > 0 | $= 0$ |

from which follows

$$S = \frac{QC^2 \varepsilon_0^2}{(T - T_c)^2} E^2. \quad (14)$$

(9) The weak-signal R-coefficient is, consequently, proportional to QC^2 , but please note that this approximation is valid only at very small maximum deformations.

3. Qualitative Discussion of the High-Signal Behaviour

A general discussion of the coefficients α , β etc. shows their difference depending on the order of the phase transition. Regarding a positive electrostriction ($Q > 0$) we get the characteristics listed in Table 1. They are divided into first and second order phase transition ($\xi < 0$ and $\xi > 0$).

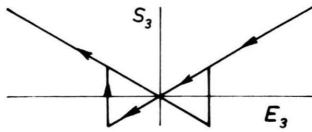


Fig. 6.
Conventional idea
of a switching curve
of a uniaxial ferroelectric.

The main difference between a first and a second order phase transition appears with respect to the β - and γ -coefficients (not to mention that μ and ν are zero in the case of a second order phase transition). Both β -coefficients change, though in an opposite way(!), their sign at T_c , the γ -coefficient, however, only in the case of a first order phase transition (but at a temperature below T_c). These differences result in a strikingly different change of the high-signal strain-field curve when the temperature decreases from the paraelectric phase and reaches the phase transition range. Figure 5 presents the corresponding qualitative evolution of the strain-field curves, as it is predicted by a discussion of (7).

The upper and lower halves illustrate first order ($\xi < 0$) and second order ($\xi > 0$) phase transitions. The temperature decreases from left to right so that the left part is the paraelectric one. The dotted lines represent those parts which are not realized. In the case of a second order phase transition it is not possible to predict the switching field strength (coercive field). In this way a small part of the lower section can be realized when the sign of the field is changed, but the sign of the spontaneous polarization still remains unchanged.

On the basis of the experimentally determined high-signal electromechanical behaviour the shown pictures permit to conclude whether the phase transition is of first or second order.

Above all, in the case of a first order phase transition a special switching hysteresis is observed within a certain temperature range above and slightly below T_c . This hysteresis indicates a field induced transition (transitional switching), respectively a retransition from a paraelectric to a ferroelectric and back to a paraelectric phase or – this is the case below T_c – a polarization reversal through an intermediate paraelectric phase. The latter case should be observable down to a temperature at which a strain-field curve like that in the middle picture of the ferroelectric phase in Fig. 5 appears. Below this temperature the normal switching behaviour occurs, which is in the case of a second order phase transition the only observable one.

Beyond that, in the case of a second order phase transition no hysteresis whatever is seen in the paraelectric phase. On the other hand, slightly above and at T_c an extraordinary shape of the strain-field curve with the character of a root function is predicted. Such a dependence, determined experimentally, was indeed presented already in Figure 3.

Independent on the order of the phase transition a special feature of the strain-field dependence attracts attention within the ferroelectric phase. This is the observed negative curvature of the unipolar part in the strain-field dependences (from the maximum field strength down to zero field) within the ferroelectric phase. Here it should be mentioned once more that only a uniaxial ferroelectric is considered. The observed curvature is consequently not a result of 90° -domain switching. This is remarkable since the conventional idea of a switching curve of a uniaxial ferroelectric (i.e. without any 90° -domain switching) is that of Figure 6 [12]. Quite on the contrary, such a negative curvature has been, up to now, ascribed to the action of 90° -domain switching or to a special switching mechanism which can only be found in relaxor type ferroelectrics [13].

Equation (7), however, yields such a curved dependence without 90° -domain switching and makes evident that a curve like in Fig. 6 can be expected only at low temperatures far from the Curie point. 90° -domain switching, of course, still increases the negative curvature of the strain-field curves as far as it appears.

With the help of (7) it is possible to estimate the influence of the electrostrictive Q - and the thermodynamical C -, ξ - and ζ -coefficients. In carrying out such an estimation, the impact of these coefficients on the formation of the high-signal electrostriction should finally be briefly discussed:

$Q \geq 0$:

A change of Q does not cause any variation in the qualitative shape of the S - E -curves. The realized strain value is also proportional to Q in the high-signal range.

$C > 0$:

A change of C does not cause any variation, neither in the qualitative nor in the quantitative shape, of the S - E -curves, but causes a shift of the temperatures at which the same S - E -curves are observed (an increasing of C increases the corresponding temperature).

$\xi < 0$ (first order phase transition):

An increase of $|\xi|$ intensifies the hysteresis and increases the strain. Therefore the ξ -coefficient is particularly important for the formation of high-signal electrostriction when the material is to be used as an electrostrictor.

$\xi > 0$ (second order phase transition):

The larger ξ , the flatter the S - E -curve and the smaller is the maximum strain (a hysteresis does not appear in the paraelectric phase).

$\zeta > 0$:

An increase of ζ causes a flattening of the S - E -curve already at lower field values (this means a decrease of the maximum strain).

The proposed method is useful and expedient to predict high-signal deformation curves (electrostrictive ones in the paraelectric and fundamental switching ones in the ferroelectric phase). A comparison with experimentally determined high-signal curves and a prediction of particularly interesting effects and their possible application is carried out in Part II.

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