acta phys. slov. 30. (1980), No. 1

NONLINEAR PROPERTIES OF PARAELECTRIC BARIUM TITANATE CRYSTALS*

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A thermodynamical model has been developed in order to calculate the temperature behaviour of linear and nonlinear elastic, dielectric and electromechanical coefficients for a phase transition of the first order. For paraelectric barium titanate crystals it is shown that the comparison of the theoretical results with the experiments provides further information on the coupling between the order parameter and mechanical stress on the one hand and the electric field strength on the other. The temperature dependence of the linear and nonlinear elastic coefficients can be explained by the assumption of a linear coupling between the order parameter and the mechanical stress, produced by polar defects.

НЕЛИНЕЙНЫЕ СВОЙСТВА ПАРАЭЛЕКТРИЧЕСКИХ КРИСТАЛЛОВ ТИТАНАТА БАРИЯ

В работе развита термодинамическая модель, позволяющая рассчитать линейное и нелинейное температурное поведение модуля упругности, диэлектрической постоянной и электромеханических коэффициентов для фазового перехода первого рода. Показано, что в случае параэлектрического кристалла титаната бария сравнение теоретических результатов с экспериментом дает возможность получения новой информации о связи между параметром упорядочения и механическим напряжением с одной стороны и напряженностью электрического поля с другой стороны. Температурную зависимость линейного и нелинейного модулей упругности можно объяснить, исходя из предположения линейной связи между параметром упорядочения и механическим напряжением, созданным полярными дефектами.

I. INTRODUCTION

The aim of the present paper is to show that the knowledge of the temperature dependence of nonlinear elastic, dielectric and electromechanical coefficients provides further information on the coupling between the order parameter and the mechanical stress on the one hand and the electric field strength on the other. Theoretic and experimental results are given for paraelectric barium titanate

* Talk given at 6[th] Conference of Ultrasonic Methods in Žilina, September 14[th]—16[th], 1978.

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crystals. The results provide new conclusions for the coupling between the order parameter and the mechanical stress.

II. THERMODYNAMICAL DESCRIPTION OF NONLINEAR EFFECTS

A number of nonlinear effects in solids can be discussed on the basis of a thermodynamical consideration. In this case the thermodynamical potential function is expanded in terms of a higher order of the mechanical stress and the electric field strength [1]. Then the equations of state for the mechanical strain S_i and the dielectric displacement D_m have the following form:

$$S_i = s_{ij}^E T_j + d_{mi}E_m + s_{ijk}^E T_j T_k + 2d_{mij}T_jE_m + R_{mni}E_mE_n + s_{ijkl}^E T_jT_kT_l + 3d_{mijk}T_jT_kE_m + 3L_{mnij}T_jE_mF_n + R_{mnpi}E_mE_nE_p$$

$$D_m = d_{mi}T_i + \varepsilon_{mn}^T E_n + d_{mij}T_iT_j + 2R_{mni}T_iE_n + \varepsilon_{mnp}^T E_nE_p + d_{mijk}T_iT_jT_k + 3L_{mnij}T_iT_jE_n + 3R_{mnpi}T_iE_nE_p + \varepsilon_{mnpq}^T E_nE_pE_q$$

Here s_{ij}^E is the elastic coefficient of the second order, d_{mi} the piezoelectric coefficient and ε_{mn}^T the dielectric constant. s_{ijk}^E is the nonlinear elastic coefficient of the third order and determines the change of the linear elastic coefficient with the mechanical stress. d_{mij} is the nonlinear piezoelectric coefficient and describes the dependence of the linear elastic coefficient of the electric field strength and the dependence of the piezoelectric coefficient on the mechanical stress. The electrostrictive coefficient R_{mni} describes the electrostriction and the dependence of the dielectric constant on the mechanical stress. ε_{mnp}^T is the nonlinear dielectric coefficient of the third order and characterizes the change of the linear dielectric constant with the electric field strength.

The nonlinear elastic coefficient of the third order and the electrostrictive coefficient exist for all crystal classes, but the nonlinear dielectric coefficient only for crystal classes without a centre of symmetry.

In the case of the nonlinear coefficients of the fourth order we want to consider the nonlinear elastic coefficient s_{ijkl}^E and the nonlinear dielectric coefficient ε_{mnpq}^T only.

III. METHODS FOR THE DETERMINATION OF NONLINEAR ELASTIC, DIELECTRIC AND ELECTROMECHANICAL COEFFICIENTS

The nonlinear elastic coefficients can be calculated from the shift of the resonance frequency of longitudinal vibrating bars in dependence of the amplitude on the driving force [2]. The same principle is used for the determination of the nonlinear dielectric coefficients. The sample is integrated in a series resonant circuit and the change of the resonance frequency in dependence of the amplitude on the driving force is measured.

The nonlinear piezoelectric coefficient is determined by the change of the resonance frequency of mechanical vibrations with the application of a dc biasing field.

A dynamical method, the so-called electrostrictive resonator, is used for the determination of the electrostrictive coefficients [3].

IV. THERMODYNAMICAL MODEL FOR THE TEMPERATURE DEPENDENCE OF THE NONLINEAR COEFFICIENTS

A thermodynamical model has been developed in order to calculate the temperature dependence of linear and nonlinear coefficients near the phase transitions of the first order. In the spirit of the Landau theory of phase transitions we start from the following thermodynamical potential function:

$$\begin{aligned} G = {} & G_0(\vartheta) - \tfrac{1}{2}s_{ij}^E T_iT_j - d_{mi}T_iE_m - \tfrac{1}{2}\varepsilon_{mn}^T E_mE_n - \tfrac{1}{3}s_{ijk}^E T_iT_jT_k - \\ & - d_{mij}T_iT_jE_m - R_{mni}T_iE_mE_n - \tfrac{1}{3}\varepsilon_{mnp}^T E_mE_nE_p - \tfrac{1}{4}s_{ijkl}^E T_iT_jT_kT_l - \\ & - d_{mijk}T_iT_jT_kE_m - \tfrac{3}{2}L_{mnij}T_iT_jE_mE_n - R_{mnpi}T_iE_mE_nE_p - \\ & - \tfrac{1}{4}\varepsilon_{mnpq}^T E_mE_nE_pE_q + \tfrac{1}{2}A_{rr}\eta_r^2 + \tfrac{1}{4}B_{rrrr}\eta_r^4 + \tfrac{1}{6}C_{rrrrrr}\eta_r^6 - K_{ri}T_i\eta_r - \\ & - \alpha_{rm}E_m\eta_r - M_{rij}T_iT_j\eta_r - \beta_{rmn}E_mE_n\eta_r - N_{rri}T_i\eta_r^2 - \gamma_{rrm}E_m\eta_r^2 - \\ & - 2V_{rmi}T_iE_m\eta_r . \end{aligned}$$

The potential function is expressed in terms of the mechanical stress T_i, the electric field strength E_m and the order parameter η_r. The coupling coefficients K_{ri}, α_{rm}, M_{rij}, β_{rmn}, N_{rri}, γ_{rrm} and V_{rmi} describe the interaction between the order parameter and the stress on the one hand and the field strength on the other. All the coefficients of the potential are considered as temperature independent with the exception of A_{rr} [4].

It is important to notice that the nonlinear elastic coefficients are determined under the condition of a constant electric field. So we have to develop the potential in powers of the electric field strength, in order to be able to compare the results of the thermodynamical model with the experiment.

For the calculation of the temperature dependence of the nonlinear elastic, dielectric and electromechanical coefficients we use the following equations:

$$\tilde{s}_{ij}^E = \frac{\partial S_i}{\partial T_j} + \frac{\partial S_i}{\partial \eta_r}\frac{\partial \eta_r}{\partial T_j} \qquad \tilde{d}_{mi} = \frac{\partial D_m}{\partial T_i} + \frac{\partial D_m}{\partial \eta_r}\frac{\partial \eta_r}{\partial T_i}$$

$$\tilde{\varepsilon}_{mn}^T = \frac{\partial D_m}{\partial E_n} + \frac{\partial D_m}{\partial \eta_r}\frac{\partial \eta_r}{\partial E_n}$$

$$\tilde{s}_{ijk}^E = \frac{1}{2}\left(\frac{\partial \tilde{s}_{ij}^E}{\partial T_k} + \frac{\partial \tilde{s}_{ij}^E}{\partial \eta_r}\frac{\partial \eta_r}{\partial T_k}\right), \quad \tilde{d}_{mij} = \frac{1}{2}\left(\frac{\partial \tilde{s}_{ij}^E}{\partial E_m} + \frac{\partial \tilde{s}_{ij}^E}{\partial \eta_r}\frac{\partial \eta_r}{\partial E_m}\right)$$

$$R_{mni} = \frac{1}{2}\left(\frac{\partial \tilde{\varepsilon}^T_{mn}}{\partial T_i} + \frac{\partial \tilde{\varepsilon}^T_{mn}}{\partial \eta_r}\frac{\partial \eta_r}{\partial T_i}\right),$$

$$\tilde{\varepsilon}^T_{mnp} = \frac{1}{2}\left(\frac{\partial \tilde{\varepsilon}^T_{mn}}{\partial E_p} + \frac{\partial \tilde{\varepsilon}^T_{mn}}{\partial \eta_r}\frac{\partial \eta_r}{\partial E_p}\right)$$

$$\tilde{s}^E_{ijkl} = \frac{1}{3}\left(\frac{\partial \tilde{s}^E_{ijk}}{\partial T_l} + \frac{\partial \tilde{s}^E_{ijk}}{\partial \eta_r}\frac{\partial \eta_r}{\partial T_l}\right),$$

$$\tilde{\varepsilon}^T_{mnpq} = \frac{1}{3}\left(\frac{\partial \tilde{\varepsilon}^T_{mnp}}{\partial E_q} + \frac{\partial \tilde{\varepsilon}^T_{mnp}}{\partial \eta_r}\frac{\partial \eta_r}{\partial E_q}\right).$$

The results of the thermodynamical model for the temperature dependence in the paraelectric phase of some linear and nonlinear coefficients are shown in Table 1.

Table 1

Temperature dependence of some linear and nonlinear coefficients in the paraelectric phase

Coefficient	Temperature dependence
$\tilde{s}^E_{ii} - s^E_{ii}$	$\frac{K^2_{ri}}{a_{rr}(\vartheta - \vartheta_0)}$
$\tilde{d}_{mi} - d_{mi}$	$\frac{\alpha_{rm}K_{ri}}{a_{rr}(\vartheta - \vartheta_0)}$
$\tilde{\varepsilon}^T_{mm} - \varepsilon^T_{mm}$	$\frac{\alpha^2_{rm}}{a_{rr}(\vartheta - \vartheta_0)}$
$\tilde{s}^E_{iii} - s^E_{iii}$	$\frac{3K_{ri}M_{rii}}{a_{rr}(\vartheta - \vartheta_0)} + \frac{3K^2_{ri}N_{rri}}{[a_{rr}(\vartheta - \vartheta_0)]^2}$

Table 2

Existing coupling coefficients for proper ferroelectrics

Coupling	Existing coupling coefficients
$K_{ri}T_i\eta_r$	d_{ri}
$\alpha_{rm}E_m\eta_r$	ε^T_{rm}
$M_{rij}T_iT_j\eta_r$	d_{rij}
$\beta_{rmn}E_mE_n\eta_r$	ε^T_{rnp}
$N_{rri}T_i\eta^2_r$	R_{rri}
$\gamma_{rrm}E_m\eta^2_r$	ε^T_{rrp}
$V_{rmi}T_iE_m\eta_r$	R_{rmi}

V. RESULTS FOR PARAELECTRIC BARIUM TITANATE

For proper ferroelectrics it is possible to make conclusions on the actually existing coupling parameters, when the point group of the symmetric phase and the direction of the spontaneous polarization are known, as shown in Table 2.

Since barium titanate is centrosymmetric in the paraelectric phase, all the coupling coefficients K_{ri}, M_{rij}, β_{rmn} and γ_{rrm} are equal to zero and we obtain the following expressions for the theoretic temperature dependence of the material coefficients, as shown in Table 3. Further we see in Table 3 the experimental results for the linear and nonlinear dielectric constants and the electronegative coefficient are in good agreement.

It is not possible to understand the temperature behaviour of the linear and nonlinear elastic coefficients, since from the symmetric point of view a linear

Table 3

Theoretic and experimental temperature dependence of some linear and nonlinear coefficients of paraelectric barium titanate

Coefficient	Temperature dependence theoretic	experimental
$\tilde{s}^E_{ii} - s^E_{ii}$	0	$\sim(\vartheta - \vartheta_0)^{-1}$
$\tilde{\varepsilon}^T_{mm} - \varepsilon^T_{mm}$	$\frac{\alpha^2_{rm}}{a_{rr}(\vartheta - \vartheta_0)}$	$\sim(\vartheta - \vartheta_0)^{-1}$
$\tilde{s}^E_{iii} - s^E_{iii}$	0	$\sim(\vartheta - \vartheta_0)^{-2}$
$\tilde{R}_{mmi} - R_{mmi}$	$\frac{N_{rri}\alpha^2_{rm}}{a_{rr}(\vartheta - \vartheta_0)^2}$	$\sim(\vartheta - \vartheta_0)^{-2}$
$\tilde{\varepsilon}^T_{mmmm} - \varepsilon^T_{mmmm}$	$\frac{-\alpha^4_{rm}B_{rrrr}}{a_{rr}(\vartheta - \vartheta_0)^4}$	$\sim(\vartheta - \vartheta_0)^{-4}$

coupling between the order parameter and the mechanical stress is not allowed and linear and nonlinear elastic coefficients have to be temperature independent.

The log-log plot in Fig. 1 shows that in a large range of temperature the change of the linear elastic coefficient is proportional to $(\vartheta - \vartheta_0)^{-1}$.

Fig. 2 shows the log-log plot of the change of the nonlinear elastic coefficient. The change of this coefficient is proportional to $(\vartheta - \vartheta_0)^{-2}$.

These two results obtained by independent methods can be explained only if a linear coupling between the order parameter and the mechanical stress is

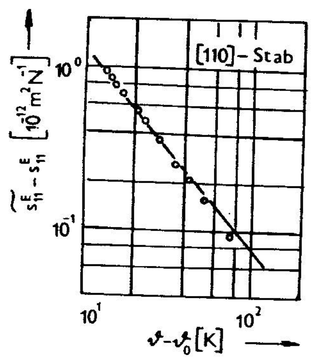

Fig. 1. Temperature dependence of the linear elastic coefficient in a log-log plot

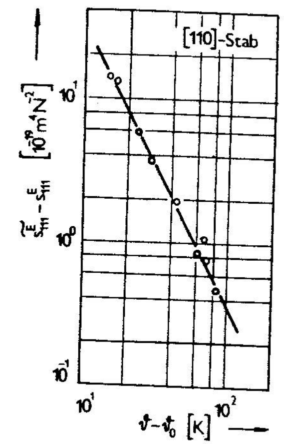

Fig. 2. Temperature dependence of the nonlinear elastic coefficient in a log-log plot

assumed. The reason for such a coupling could be the influence of polar defects in the real crystal. The fact that it is possible to measure in the paraelectric phase a dielectric nonlinearity of the third order, as shown in Fig. 3, indicates the existence of polar defects in the crystal.

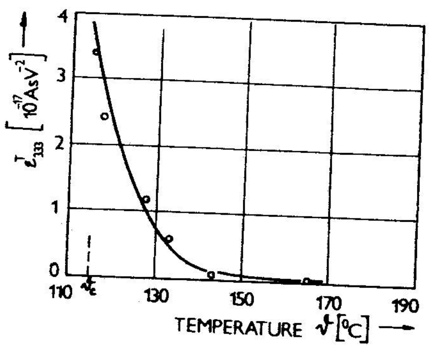

Fig. 3. Temperature dependence of the nonlinear dielectric coefficient of the third order

VI. CONCLUSIONS

The measurements show that the knowledge of the temperature behaviour of nonlinear elastic, dielectric and electromechanical coefficients provides further information for the understanding of phase transitions. It is very useful to compare the theoretic results with the experiments. In the case of paraelectric barium titanate we come to the conclusion that the polar defects produce a linear coupling between the order parameter and the mechanical stress. By the existence of this coupling we can understand the temperature behaviour of the linear and nonlinear elastic, dielectric and electromechanical coefficients.

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Received October 19th, 1978