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Investigations of the elastic behaviour in the vicinity of ferroelectric phase transitions*

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Abstract

Experimental methods are briefly summarized. A survey of anomalies of elastic coefficients in the vicinity of ferroelectric phase transitions and of the acoustic attenuation is given. New trends in research concerning cluster- and glass-like behaviour are also considered.

1. Introduction

Ferroelectrics belong to the class of solid state materials which undergo distortive structural phase transitions. A first description of the physical properties and their changes can be performed with the use of the Landau theory of phase transitions if the transition itself is not far away from second order. For a better understanding further theories and models such as, for example, mean field theory, renormalization group theory and the soft mode concept have to be applied. From the physical point of view the unusual extreme behaviour of some properties of substances with ferroelectric phase transitions near their transition point is interesting and has been widely studied. Applications use the high dielectric permittivity and large electromechanical coefficients.

We distinguish the following kinds of ferroelectrics.

(1) *Proper ferroelectrics*. The spontaneous polarization P_s is the order parameter.

(2) *Pseudoproper (weak) ferroelectrics*. The spontaneous polarization is only linearly coupled with the order parameter.

(3) *Improper ferroelectrics*. The phase transition must be described by an order parameter with more than one component. (The number of cell parameters will be multiplied.)

(4) *Ferroelectrics with commensurate–incommensurate phase transition*. The incommensurate phase exists in a temperature interval above the ferroelectric phase. The order parameter depends on the spatial coordinates.

(5) *Relaxor ferroelectrics*. They exhibit a broad frequency-dependent maximum of the dielectric permittivity that shifts to higher temperatures with increasing frequency.

On the basis of an atomic single potential a distinction between an order–disorder and a displacive transition is possible. The acoustic behaviour also depends on the type of the transition (first or second order).

2. Methods for investigations of elastic properties

Complex elastic properties are determined by direct measurements of linear and non-linear coefficients as well as of the ultrasonic attenuation and of the mechanical quality and internal friction respectively as a function of the temperature, the frequency and various other external parameters such as electric fields or mechanical stresses. Several methods for this purpose are presented in Table 1. A general discussion of many methods is given in ref. 1.

Methods of probing elastic properties of ferroelectrics range from quasi-static methods to dynamic methods performed in the gigahertz range. Ultrasonic methods have the greatest variety. The whole tensor of stiffness coefficients can be determined in principle by these methods. A direct comparison of the elastic compliances s_{ij} with the elastic stiffnesses c_{ij} is often complicated because of the lack of some s_{ij} components that are in some cases not measurable. It should be noted that the attenuation has the dimension of reciprocal length but the internal friction is dimensionless.

Any discussion of the results must take boundary conditions into consideration. These are for ferroelectrics measurements at constant polarization or constant electric field and adiabatic or isothermal condition [6, 7].

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TABLE 1. Methods for the investigation of elastic properties

Method	Frequency range (Hz)	Elastic coefficient	Loss
Torsion pendulum	10^{-4}–10	c_{ij}	Internal friction [2]
Longitudinal strain measurement	10^{-4}–10^2	s_{ij}	Mechanical quality [3]
Resonance–antiresonance	10^4–10^6	s_{ij}	Mechanical quality [4]
Ultrasonic methods	10^6–10^9	c_{ij}	Attenuation
Hypersonic methods	10^9–2×10^{10}	c_{ij}	Attenuation
Brillouin scattering	10^8–10^{10}	c_{ij}	Attenuation [5]
Inelastic neutron scattering	10^{12}	c_{ij}	

3. Statement on elastic measurements

The properties of the real parts of the elastic coefficients are to a first approximation determined by static effects. Dynamic effects such as the fluctuation and the relaxation of the polarization influence mainly the imaginary parts. The elastic behaviour in the vicinity of phase transitions may be described in principle by a coupling of an acoustic mode with the ferroelectric soft mode. The crystal symmetry determines the possible coupling; in particular, piezoelectric and electrostrictive couplings are observable. Methods presented in Table 1 give information on the bulk properties in four main directions.

(1) The defect structure of ferroelectrics is determined through its response to the influence of elasticity. Known models [8–10] are combined with phenomena arising during the transition, *e.g.* ferroelectric domains.

(2) Research looks for information on the critical behaviour near the phase transition.

(3) Investigations concerning the non-linear elastic behaviour in the neighbourhood of the phase transition are also performed in order to obtain data for technical reasons and applications (thin films).

(4) Resonance and relaxation phenomena are investigated using measurements of acoustic dispersion. They can give information on the internal mechanisms of elastic and related problems, on glass-like behaviour [3] or on special cluster interaction mechanisms [11]. The elastic behaviour of strontium titanate is shown as example in Fig. 1. Dispersion measurements can contribute to answering the following question: why are elastic anomalies often observable only at low frequencies or more pronounced than at higher frequencies?

We prefer combined measurements, *e.g.* of elastic compliances and thermal expansion simultaneously as a function of temperature and electric fields.

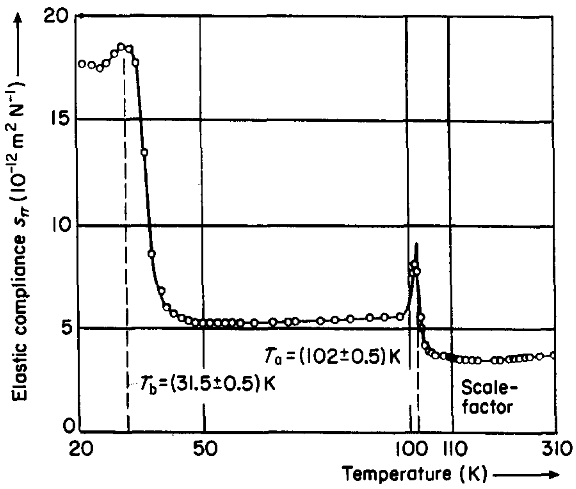

Fig. 1. Temperature dependence of the elastic compliance of strontium titanate.

4. On the temperature dependence of linear elastic coefficients

We use the Landau free energy F which describes the behaviour of the elastic stiffness coefficients:

$$F(S_k, T, P_i) = F(T) + \frac{A}{2}(T)P_i^2 + \frac{B}{4}P_i^2 + \frac{C}{6}P_i^6 + F_c \quad (1)$$

where F_c is the coupling energy given by

$$F_c = \beta_{ij}P_iS_j + \gamma_{ijk}P_iP_jS_k + \delta_{ijk}P_iS_jS_k \quad (2)$$

P_i denotes an order parameter component, T is the temperature, B and C are constants and A follows the linear relation $A = A'(T - T_c)$. T_c is the critical temperature and coincides in the case of a phase transition of second order with the Curie temperature. The term $F(T)$ is the free energy in the paraphase.

The coupling energy contains a term of bilinear coupling between order parameter and strain S_j, which displays a piezoeffect for proper ferroelectrics. The higher coupling terms are strictive couplings. This theme is described in more detail for instance by Rehwald [12] and others [13–16]. Corresponding to the possible coupling three different acoustic anomalies are expected at the phase transition: peaks that fulfil the Curie–Weiss law if only $\beta_{ij} \neq 0$, steps (if only $\gamma_{ijk} \neq 0$) and a temperature dependence proportional to the spontaneous value of the polarization if only $\delta_{ijk} \neq 0$. The temperature dependences of the elastic compliance coefficients are "qualitatively inverse". Crystal imperfections, fluctuations of the order parameter and non-classical phenomena close to T_c can change the above-mentioned step into a power law, that can be described by a critical exponent.

Over the last few years considerable attention has been attracted to phenomena in a new class, so-called "weak" ferroelectrics. The model of weak ferroelectrics included the model of pseudoproper ferroelectrics [17–19]. The soft modes are weakly polar and possess an anomalously low effective charge. The Curie–Weiss constant and the spontaneous polarization in these crystals are very small. Tris sarcosine calcium chloride (TSCC) is one of these substances. The elastic behaviour of TSCC is displayed in Fig. 2. Substantially we find the same anomalies of the elastic moduli as in proper ferroelectrics. Furthermore, the temperature range where the fluctuations contribute to elastic moduli is unusually large [20].

Improper ferroelectricity is possible only when the order parameter (in most cases atomic displacements) is a multicomponent parameter. The spontaneous polarization is proportional to the temperature difference $T_c - T$ in the polar phase. The phase transition temperature is shifted with an applied electric field [21]. This is seen as well in elastic as in dielectric properties. The transitions are in most cases of first order or near second order and the thermodynamic potential therefore must contain invariants of sixth order. It is impossible to conclude with only elastic measurement data whether an improper ferroelectric transition exists in the given case.

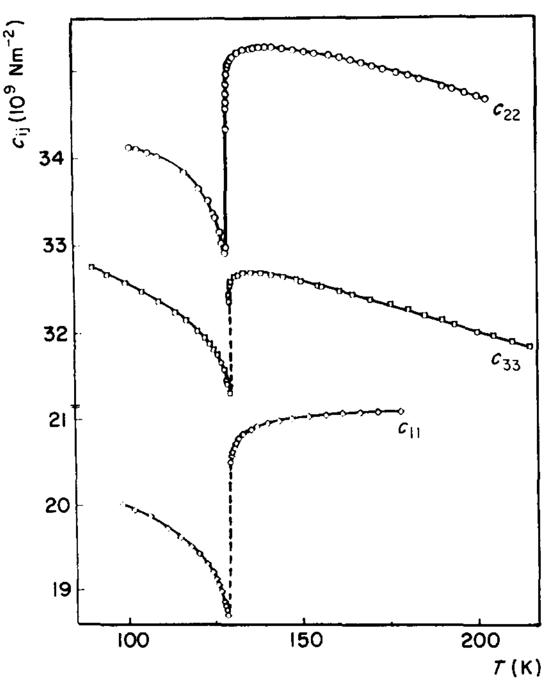

Fig. 2. Temperature dependences of the elastic stiffnesses c_{11}, c_{22} and c_{33} of TSCC.

In ferroelectrics with incommensurate phases the same extension concerning the Landau theory is made but the order parameter varies in space as a periodic function incommensurate with the lattice. Three temperature ranges with different acoustic anomalies are observable. T_i denotes the phase transition temperature from the paraelectric to the incommensurate phase. Above this temperature acoustic anomalies are due to a coupling between an acoustic and a soft mode. All acoustic anomalies below T_i are due to a coupling between an acoustic mode and the so-called amplitudon and phason branches of the soft mode. A further coupling type only leads to a dip [22, 23] as in ammonium fluoberyllate (Fig. 3). The "devil's staircase" in the k $vs.$ T curves is also observable with small elastic dip anomalies [24]. The transition from the incommensurate phase into the ferroelectric phase is characterized by a lock-in of the incommensurate modulated order parameter into a commensurate value and the temperature is denoted by T_c. Around T_c only a dip is expected and measured. No general theory has yet been worked out for this region. An interesting aspect is the asymmetric behaviour of some transverse acoustic waves. Esayan and Lemanov [23] found a difference between sound velocities in a certain temperature region that should be identical from the crystallographic point of view.

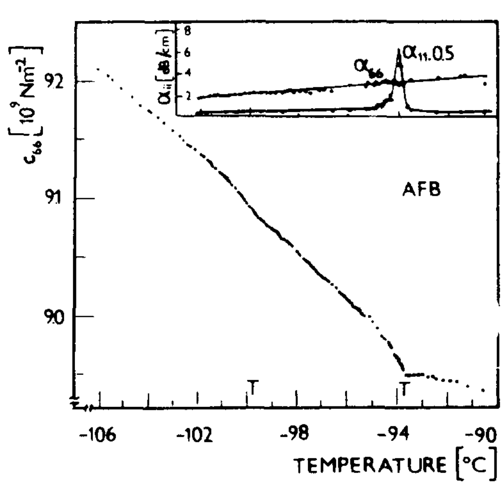

Fig. 3. Temperature dependence of the elastic stiffness coefficient c_{66}, of the corresponding attenuation α_{66} and of the attenuation α_{11} in ammonium fluoberyllate.

The broad maximum of the dielectric permittivity in relaxor ferroelectrics is connected with a broad maximum of the elastic compliances. Both physical quantities exhibit the same relaxation behaviour in the frequency and in the time domain [25].

5. Non-linear elastic coefficients

There are some methods for the measurement of elastic non-linearities such as the generation of harmonics of ultrasound, the application of mechanical stress or pressure to the solid sample and the determination of the shift of the resonance frequency of the piezoelectric resonator [15]. Perhaps the non-linear properties are assigned a greater importance because the knowledge of their temperature behaviour provides further information and they are a more sensitive indicator for the microscopic changes in the vicinity of phase transitions than the linear coefficients [26].

6. Acoustic damping

Dissipative processes must be considered if elastic coefficients are determined via the sound velocity and not directly. The imaginary part of these coefficients represents the ultrasonic attenuation. In many cases the order parameter response can be explained by a relaxation process. Landau and Chalatnikov [27] created a model assuming that the rise of attenuation may be attributed to an increase in the relaxation time of the order parameter. Dispersion effects at very high frequencies as in Brillouin scattering are due to order parameter relaxation while at low ultrasonic frequencies domain wall relaxation plays the most important role. At infralow frequencies the damping depends on crystal lattice imperfections (point defects, dislocations, domain and interphase boundaries) [28]. It is important to determine whether the damping arises as a result of intrinsic mechanisms or imperfections. Cluster effects are of interest too. Effects caused by domains have been studied as a function of external fields. Levanyuk constructed a theory which is based on the interaction of sound waves with thermal fluctuations of the order parameter [29]. He made the assumption of a quadratic dependence of the deformation from the order parameter. As a result substantial fluctuations are responsible for the damping above the ferroelectric phase transition and below it relaxation processes are most important. From further models explaining the attenuation anomalies [23, 30] we mention first that of Nattermann [30], who took into account a strictive coupling in the potential and obtained logarithmic laws for the anomalous attenuation. A model from Esayan and Lemanov was developed for the explanation of the attenuation anomalies in incommensurate phases and this reveals also a strong influence of the wave type and the propagation direction on the attenuation. Bamberg and Schmidt published a model to explain the attenuation in diffuse ferroelectrics that works with interacting microdomains [31].

7. Conclusion

Sound velocity, attenuation and dispersion provide essential information on ferroelectric phase transitions. Elastic coefficients and the damping are very sensitive to the phase transition. The results allow the construction of phase diagrams and give information on the type of the phase transition, on the coupling of the order parameter to other modes allowed by the symmetry and on the dynamics of the order parameter.

Much has to be done in the field of the interpretation of the frequency dependence of elastic coefficients and the attenuation. It should be possible to obtain from these sources more information on the damping mechanisms and glass-like behaviour as well as on the consequence of intrinsic properties due to imperfection and clusters.

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