ULTRASONIC INVESTIGATIONS OF STRUCTURAL PHASE TRANSITIONS[1])

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The aim of the paper presented is a description of the present status of investigations of structural phase transitions using ultrasound methods, including some remarks concerning modern trends of elastic investigations of such phase transitions.

УЛЬТРАЗВУКОВЫЕ ИССЛЕДОВАНИЯ СТРУКТУРНЫХ ФАЗОВЫХ ПЕРЕХОДОВ

В работе приводится обзор современного состояния исследований структурных фазовых переходов при помощи ультразвуковых методов. Приводятся комментарии к современным направлениям исследований в области указанных фазовых переходов.

I. INTRODUCTION

The investigation of the physical behaviour of solids under extreme conditions is one of the modern trends of solid state physics. By such investigations we generally mean measurements at highest pressure, at the strongest applied electric and magnetic field, lowest temperatures, samples of highest achievable purities, aimed at internal disturbances and measurements after irradiation. On the other hand, the unusual behaviour of substances with phase transitions near their transition points is being studied: Lowest external influences or internal disturbances or defects already cause considerable changes in their physical behaviour. We will only deal with structural distortive phase transitions in this paper. The displacements of the lattice elements at structural distortive phase transitions are small — in comparison with interatomar distances. In such a case a sufficient description of physical properties or their changes with the help of Landau's theory of phase transitions is possible excluding the closest range to the transition itself (temperature deviation less than 0.1 K).

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Experiments dealing with elastic properties are widely used in the investigation of phase transitions. Such experiments consist of the direct measurement of the linear and nonlinear elastic stiffnesses c_{ij}, c_{ijk} resp., compliances s_{ij}, s_{ijk}, s_{ijkl}, the ultrasonic attenuation α_{ij} and the mechanical quality Q_{ij} in dependence on external parameters. With measurements of the acoustic dispersion resonance and relaxation phenomena are investigated. Several methods have been devised for this purpose (see Table 1).

Table 1

Experimental methods for investigations of elastic coefficients and attenuation

method	frequency range [Hz]	elastic coefficient	loss
torsion pendulum	10^{-4} ...... 10 Hz	c_{ij}	quality [1]
resonance-antiresonance	10 KHz .... 1 MHz	s_{ij}	quality [2]
ultrasonics	1 MHz .... 1 GHz	c_{ij}	attenuation
hypersonics	1 GHz ... 20 GHz'	c_{ij}	attenuation
Brillouin scattering	100 MHz ... 10 GHz*	c_{ij}	attenuation [3]

* depends on scattering geometry

With these methods a frequency range of 10^{-4}—10^{10} Hz is available. The ultrasonic and hypersonic methods have the largest frequency range among these methods and have the greatest variability.

The whole tensor of elastic coefficients may be determined on principle by these methods. A direct comparison of the s_{ij} coefficients determined by resonance measurements with c_{ij} coefficients is often complicated because of the lack of s_{ij}-tensor components which are often not all definable.

II. STATEMENTS ON ULTRASONIC MEASUREMENTS CONCERNING THE PROBLEM OF PHASE TRANSITIONS

What statements can be made from ultrasonic experiments with respect to the problem of phase transitions? The knowledge of the temperature pressure and field dependence of the sound velocity and attenuation values are useful. The properties of the sound velocity are in a first approximation determined by static effects. Dynamic effects — like the fluctuation of the order parameter — influence mainly the attenuation. Acoustic behaviour, acoustic anomalies were in principle described by the coupling of the acoustic mode with other modes (acoustic, soft modes, etc.). The symmetry determines the possible coupling.

The acoustic soft modes in ferroelastics can be measured directly in the following way. By determining the soft mode the reaction of the order parameter to external influences (like mechanical stresses or elastic fields) is examined. Ultrasonic methods give information on the bulk properties of a substance contrary to methods determining local properties like EPR, NMR. One aim of the present research is to connect macroscopic results and conceptions with microscopic ones [4].

Ultrasonic experiments in this field in the last few years point in three main directions:

I. Information from the deffect structure of solids is being obtained through its response to elastic influences. Known models (the Snoek model [5], grain boundaries as a reason of elastic scattering [6], the Granato-Lücke models [7]) are combined with phenomena arising during the transition, especially the existence of elastic as well as electric domains.

II. For technical reasons data are being obtained on the nonlinear elastic behaviour also in the neighbourhood of the phase transition.

III. Researches are looking for information on the critical behaviour near phase transitions. Review articles present already the expected and indeed observed temperature behaviour of linear elastic coefficients [8, 9]1 Schwabl gave a review talk about the present status of the theory [10].

III. ON THE DEFINITION OF ELASTIC MATERIAL QUANTITIES

If a definite property describing material quantity depends on the strength of the influencing quantity itself, we deal with nonlinear behaviour. Defining for example T_j — the mechanical strain — as the reacting quantity, we get

$$S_i = s_{ij}T_j + s_{ijk}T_jT_k + s_{ijkl}T_jT_kT_l + \dots .$$

Neglecting all coefficients s_{ijk} and s_{ijkl} the material is treated as linear. If some coefficients s_{ijk} or s_{ijkl} are nonzero, the ratio of the reacting quantity to the influencing quantity depends like

$$\frac{\partial S_i}{\partial T_j} = s_{ij} + 2s_{ijk}T_k + 3s_{ijkl}T_kT_l$$

on the influencing quantity itself. This material has nonlinear properties of third and higher orders. s_{ij} and c_{ij} are linear elastic coefficients (compliances and stiffness coefficients), and the other coefficients are nonlinear of third, fourth and higher orders. If the mechanical stress is low, the use of linear material quantities is sufficient:

$$c_{ij} = \frac{\partial^2 F}{\partial S_i \partial S_j} = \frac{\partial T_i}{\partial S_j}, \qquad s_{ij} = \frac{\partial^2 G}{\partial T_i \partial T_j} = +\frac{\partial S_i}{\partial T_j}.$$

Here the relations $S_i = \partial G/\partial T_i$, $T_i = \partial F/\partial S_i$ are used. G denotes the free elastic enthalpy, F the free energy.

For the third order coefficients, for example, there result the following relations

$$c_{ijk} = \frac{1}{2}\frac{\partial^3 F}{\partial S_i \partial S_j \partial S_k} = \frac{1}{2}\frac{\partial^2 T_i}{\partial S_j \partial S_k} = \frac{1}{2}\frac{\partial c_{ij}}{\partial S_k}$$

and

$$s_{ijk} = -\frac{1}{2}\frac{\partial^3 G}{\partial T_i \partial T_j \partial T_k} = \frac{1}{2}\frac{\partial^2 S_i}{\partial T_j \partial T_k} = \frac{1}{2}\frac{\partial s_{ij}}{\partial T_k}$$

Hence the third order elastic coefficients describe the variation of the linear elastic coefficients with deformation resp. stress. They react in some cases in a more sensitive way on internal mechanical stresses or deformations and they are more suitable as real structure influences than linear coefficients.

In tensor notation the Hookes law shows the following form

$$S_{ij} = \sum_{k,1} s_{ijkl} T_{kl} \text{ and } T_{ij} = \sum_{k,1} c_{ijkl} S_{kl} \,.$$

The connection of the tensor description and the mainly used matric descriptions is given by the following abbreviation

$$ij \rightarrow m = i \text{ if } i = j \text{ and } ij \rightarrow m = 9 - i - j \text{ if } i \neq j \,.$$

In many cases nonlinear elastic coefficients are also strongly influenced by phase transitions.

IV. GENERAL REMARKS ABOUT MEASURING TECHNIQUES FOR THE DETERMINATION OF ELASTIC QUANTITIES INCLUDING LOSSES IN SOLIDS

There exists a great variety of ultrasonic methods for the determination of elastic quantities. A survey is given by H. F. Pollard [11]. Both cw and pulse techniques are used for this purpose. The Bolef and Menes Q-meter method as an example for cw methods works with a standing wave pattern [12]. In piezoelectric resonator methods bars and plates are excited piezoelectrically. The mechanical resonance is displayed in the sample current resonance curve. The mechanic compliance s_{ij} and quality Q are found from maximum frequency and bandwidth resp.. Nonpiezoelectric samples may be measured by a composite resonator method [2].

Bulk waves impulse methods with a reflecting end with echoseries (sing-around [13], the McSkimin-method [14], impulse overlap [15], modulation method for measurement of nonlinearities [16], use of ultrasonic harmonic generation) are most widely used. The samples must be plane and parallel within 1/10 of the ultrasonic wavelength. Quartz or lithium niobate cuts are cemented to the crystal or ZnO-films are sputtered as transducers.

At hypersonic frequencies the ultrasonic wave is generated and received directly through wave guiding systems [17]. Nonpiezoelectric materials have to be coupled acoustically to generator and receiver crystals. With ultrasonic spectroscopy techniques a simultaneous measurement of the dispersion of sound velocity and attenuation can be performed. The results agree well with those obtained by measurements at discrete frequencies [18].

A new branch for the acoustical research of phase transitions are perhaps surface waves. Contrary to interdigital transducers [19] which can only be applied to piezoelectric materials, edge bounded transducers may be used for all types of crystals. (Results on surface wave propagation in crystals near their ferroelectric phase transition are given in [20]).

Furthermore there exist opto-acoustical methods making the most of the diffraction of light in ultrasonic waves in solids. Especially the method designed by Strukov et al. Allows to measure sound velocity and attenuation almost at one point in the crystal (laser system) [21]. An advantage is also the independence of the results from the used acoustical contact cement.

Phonon echo methods of piezoelectric crystals and powders may be also classed among ultrasonic techniques [22]. Elastic and piezoelectric nonlinearities of the solid state samples play the main role in the occurrence of this effect. The useful application of this effect for the improvement of attenuation measurements even in nonpiezoelectric crystals is shown in [23].

There exists a relative new modulation method [16] besides static methods for the evaluation of third order elastic coefficients. If the force influencing the sound velocity (transit time) is an electric field the nonlinear elastic coefficient is measured. If mechanical stresses are acting, the third order elastic coefficient will be obtained. By providing low attenuation relative sound variations of 10^{-7} can be detected [24].

V. ON THE TEMPERATURE DEPENDENCE OF LINEAR ELASTIC COEFFICIENTS

The description of the physical behaviour of elastic coefficients, their dependence on temperature, pressure and electric field is based on the Landau theory and renormalization group calculations. The state of a crystal is characterized by thermodynamic potentials in phenomenological thermodynamics. The choice of the type of the thermodynamic potential has to be carried out accounting by the experiment for the given independent quantities. Only electric and mechanic quantities of state must be used in the potential for our purpose. We have chosen two potentials, the free elastic enthalpy density $G(T_k, Q_i, \vartheta, P_i)$ and the free energy density $F(S_k, Q_i, \vartheta, P_i)$, where S_k is the mechanical stress, Q_i the order parameter component, ϑ the temperature and P_j a component of polarization, and neglect magnetic and other energy contributions. The desired potential should declare such temperature dependencies as: jumps, bends, peaks and so on [8, 9]. Quasi-one-dimensional systems have been lately in the centre of interest. The quasi-one-dimensional character of fluctuation dispersion leads to new effects in the behaviour of ultrasonic velocity and attenuation [25].

If one component of a linear combination of components of the strain tensor is the order parameter, we deal with proper ferroelastics. Ultrasonic investigations of the corresponding sound velocity play the same role in ferroelastics as the measurement of the dielectric susceptibility in proper ferroelectrics. With sound velocity measurements in proper or pseudoproper ferroelastics the direct measurement of the soft mode or the related Curie-Weiss-law is possible [10].

Petzelt gave a first survey of acoustic anomalies in incommensurate phases or crystals [26]. He showed that in the incommensurate transition the acoustic anomalies are qualitatively the same as those of the normal structural transitions of related types.

But anomalies of a new type can occur due to a bilinear coupling with the phason branche during the transition in commensurate incommensurate dip inelastic coefficients (and a peak in α).

Scott [27] published a survey of acoustic phonon dispersion at ic phase transitions in 1982. Both transverse and longitudinal acoustic modes exhibit such a dispersion. The LA modes have a shorter relaxation time ($BaMnF_4$: 10^{-10} s) than the Ta modes (10^{-9} s). Different relaxation times are found for different systems. Some aspects of these problems are not yet clear.

VI. NONLINEAR ELASTIC COEFFICIENTS

As we have mentioned one possibility for the determination of nonlinear coefficients is the application of mechanical stress or pressure to the solid. This possibility immediately follows from the definition of the elastic coefficients of higher order and allows to determine the whole scheme of coefficients.

Some problems still remain unsolved in the production of a sufficiently strong and homogeneous mechanical uniaxial stress state. This method also contributes big minimal sample dimensions [28].

The nonlinear elastic coefficients experimentally found are mixed isothermal-adiabatic quantities and only a complicated computation allows to convert the values to pure isothermal, resp. pure adiabatic values. But in most cases the difference is less than the measuring accuracy.

The temperature dependency of all the elements of the third order elastic coefficient tensor c_{ijk} may be calculated on principle [29]. But the experimental determination of these coefficients is difficult because the effect of nonlinear elastic coefficients appears only in a combined form and as many measurements of

coefficients as the number of existing coefficients in the corresponding point group are needed. An overestimated system of equations normally is preferred for accuracy reasons.

Therefore, only measurements of third order elastic coefficients at some fixed temperatures are known so far [30]. Dealing with resonance measurements the problem is not as complicated because of the possible linear treatment of sample vibrations [2]. On the other hand not all nonlinear compliances are measurable.

Elastic nonlinearities may be also measured using the generation of harmonics of ultrasound (electrically [31], with capacitive receiver [32]).

VII. SOME REMARKS CONCERNING ATTENUATION

Phase transitions are always connected with anomalies of the attenuation coefficients but in crystalline solids only in distinct accoustic wave propagation directions determined by crystal symmetry and order parameter.

For the description of the temperature dependence of attenuation coefficients in phase transition of second order several models have been created, e.g. the model of Landau and Chalatnikov [33]. They assume that the rise of attenuation may be attributed to an increase in relaxation time of the order parameter. In other words the deformation created by the sound wave changes the equilibrium state of the order parameter, e.g. P, the polarization of proper ferroelectrics. In the absence of linear coupling between order parameter and deformation the Landau-Chalatnikov theory supplies no anomaly. This is the case, e.g., of crystals with a centrosymmetric paraphase. For these crystala Levanyuk developed a theory accounting for the interaction of sound waves with thermal fluctuations of the order parameter [34]. It is based particularly on the assumption of a quadratic dependence of deformation on the order parameter.

A model of Nattermann based on the Larkin-Khelnitzki theory for static critical behaviour used a coupling of the kind Q^2S_{ij} or Q^2T_{ij} in the potential and gets logarithmic laws for anomalous attenuation [35].

Considerations of the critical behaviour of the sound velocity and attenuation play a more and more important role [10, 35]. Recently models for explaning the attenuation anomalies in incommensurate and diffuse phase transitions have been in the centre of interest [27, 36]. Ultrasound measurements of materials which show a diffuse phase transition as a function of temperature and of the electric field, as well as other properties (for example the remanent polarization) are in progress. The first models based on interacting microdomains offer an explanation [37].

However, there are further contributions to the damping temperature dependence that must be accounted for. Perhaps imperfections or defects also lead to phase transition independent damping effects, disregarding domain effects (especially ferroelastic ones). There are tendencies today to considers also effects of point defects, grain boundaries, dislocations and further defects (deuteration, irradiation). Models of some effects have been already long known (Snoek, elastic scattering, Granato-Lücke) but they have not been applied to the region surrounding phase transitions directly. Thus it has been tried to prove the frequency dependence of the attenuations in order to get information on the character of the attenuation. It is important to determine whether the damping arises due to intrinsic mechanisms or due to imperfections.

Especially relaxation and resonance effects have been investigated with all available methods, because the frequency behaviour gives much information on the damping mechanisms. Domain effects have been studied with the use of external fields (electric, mechanical ones).

VIII. CONCLUSIONS

The statements show that velocity, attenuation and dispersion measurements by ultrasound give essential information on phase transitions. Elastic coefficients are very sensitive to phase transitions. Their measurement allows to construct phase diagrams and give information upon the type of phase transition (transition temperature, hysteresis) and on the symmetry and the dynamics of the order parameter in elastic phase transitions. Last but not least their temperature dependence is connected with the coupling and the symmetry of the order parameter.

Statements concerning the critical behaviour and cross-over phenomena can be made. Elastic investigations are of major importance in ferroelastic phase transitions because elastic coefficients reflect directly the behaviour of susceptibility or reciprocal susceptibility comparable to the role of the dielectric coefficient in ferroelectrics.

Much remains still to be done as regards the interpretation of frequency dependences of elastic coefficients and attenuation, because it should be possible to obtain from the frequency behaviour of these quantities some information on the damping mechanisms as well as on the consequence of intrinsic properties due to imperfections.

Nonlinear elastic coefficients behaviour and defect structure are also new fields of investigation.

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