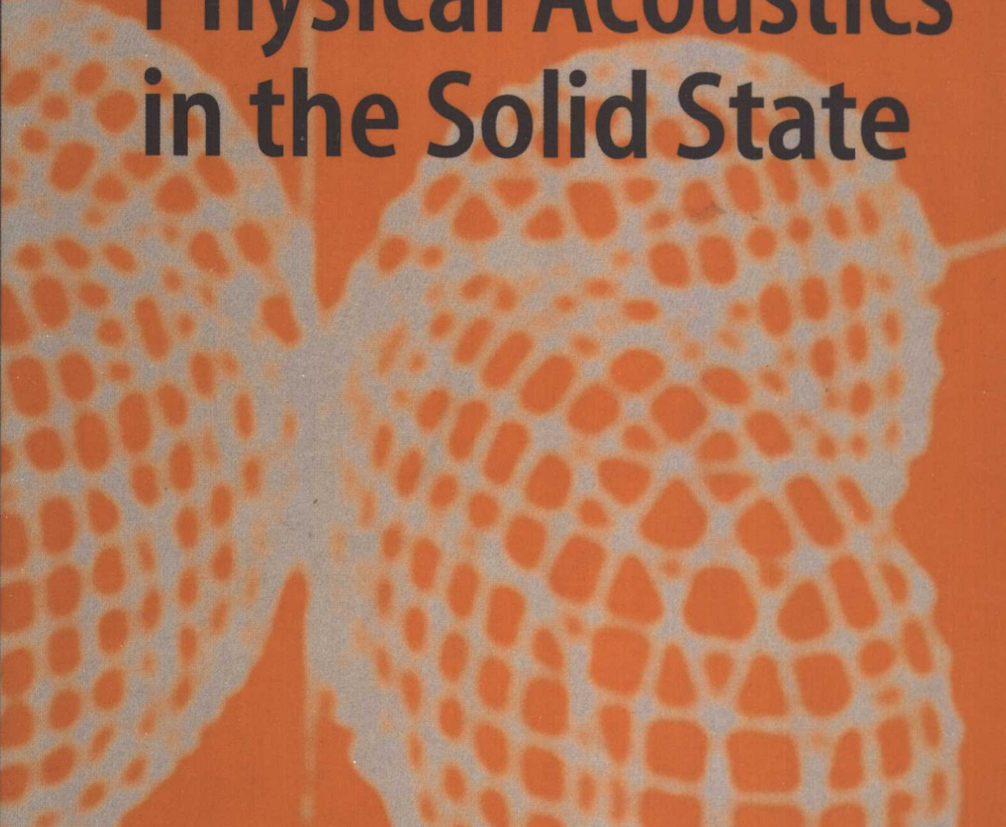
SOLID-STATE SCIENCES

B. Lüthi

Physical Acoustics in the Solid State



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Physical Acoustics in the Solid State

With 188 Figures

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Preface

This book gives an up to date survey of acoustic effects in the Solid State. After a review of the different experimental techniques and an introduction to the theory of elasticity, emphasizing the symmetry aspects, applications are given for the different fields of condensed matter physics. These applications include metals and semiconductors, superconductivity, unstable magnetic moments including heavy fermion physics, magnetism, structural and magnetic phase transitions, low dimensional systems, amorphous systems and symmetry related experiments. The main emphasis is on more recent developments not covered in books written 30 years ago. Actually, acoustic experiments have been performed in all modern fields of solid state physics.

Acknowledgments

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Frankfurt am Main, July 2004 *Bruno Lüthi*

Contents

1 Introduction

Books on physical acoustics are numerous. A series of volumes on "Physical Acoustics, Principles and Methods" by W.P. Mason [1.1] and later editors have been available since 1964. In addition, there are monographs on the same topics: "Ultrasonic Methods in Solid State Physics" by Truell et al. [1.2], "Physical Ultrasonics" by Beyer and Letcher [1.3], "Microwave Ultrasonics in Solid State Physics" by Tucker and Rampton [1.4]. But since these latter books were written more than 30 years ago, it is time to present a new account of the field.

The precise aim of this book is to present a modern account of the field. The emphasis is also slightly changed. The aspects of traditional elasticity theory are only treated briefly since they can be found in the books and treatises mentioned above and in books devoted solely to elasticity. Examples of such books are Love [1.5], Kolsky [1.6] and the standard texts on theoretical physics such as Landau Lifshitz [1.7] etc. Physical acoustics embraces the measurements of ultrasonic velocity and attenuation. The elastic constants can be gained from the ultrasonic velocities. The elastic constants are thermodynamic derivatives, the second derivative of the free energy with respect to the strains. Therefore, they are connected with the atomic and molecular bonding in the crystal. They are important, together with the specific heat and thermal expansion, for the equation of the state of a material. On the other hand the attenuation, as a transport coefficient, is connected with dissipation. It is affected by defects and inhomogeneities of the solid and more fundamentally by conduction electrons, inner (f-)electrons, thermal phonons and other relaxation processes.

This book aims to show what can be learnt about "solid state physics" using ultrasonic waves. Therefore the main objects of investigation are fields such as electron–phonon coupling in metals and semiconductors, ultrasonic effects in superconductors, spin–phonon interaction in paramagnetic and magnetic systems, phonon coupling to collective excitations and sound propagation effects near phase transitions. Of course, modern aspects of all these effects are specially treated at the expense of older treatments. The symmetry aspects are emphasized whenever possible.

Since the late 1960s and early 1970s, new fields in solid state physics have appeared. Examples are "low dimensional physics", including "low dimensional spin physics", or "unconventional superconductivity", or new types of structural phase transitions like "charge ordering" and "cooperative Jahn–Teller transitions" or "mixed valency and heavy fermions" and finally the exciting field of two-dimensional electron systems, including the quantum Hall effect, and others. These new topics, in which ultrasonics has also played an important role, will be treated in detail. In semiconductors, there are the heterostructure materials GaAs/GaAlAs which exhibit integer and fractional quantum Hall effects. For the latter case, surface acoustic waves played an important role in characterising ground and excited states. Finally much work has been done in characterising non-crystalline solids with ultrasound. The important experiments done with ultrasonics for tunneling state systems in various materials, crystalline and non-crystalline, such as glasses will be discussed briefly.

All these new topics listed can be put together under the title "highly correlated electronic systems". Whereas in former years in Solid State Physics, single particle phenomena were mainly studied, in recent years the focus has shifted to correlated electronic systems. It is therefore important to know what can be learned about these systems with ultrasonic methods. Various chapters in this book focus especially on this topic (Chaps. 7, 9, 10, 12–14).

On viewing the table of contents, it can be seen that virtually all sections of solid state physics occur in this book, indicating that acoustic techniques play an important role in this part of physics. It should also be mentioned what has been left out of this book. From the title of the book, it is clear that of the whole area of condensed matter physics it is only the solid state which is being treated. Important fields, like the liquid state, have been left out. In the liquid state, there are various subjects where ultrasonics plays an important role: Liquid Helium as He^4 or He^3. In these quantum liquids, acoustic experiments played a decisive role in determining and interpreting the different phases (see e.g. Vollhardt and Wölfle [1.8]). Another important field in the liquid state is that of liquid crystals, where ultrasonics again made important contributions in the so-called nematic, cholesteric and smectic liquid crystals (see e.g. Stephen and Straley [1.9], de Gennes and Prost [1.10]). Other topics related to ultrasonics and microwave acoustics are the different methods of studying transport properties with the use of ballistic heat pulses. This technique has widespread applications, especially for well-characterised insulators. Contact with this field will be rare. Reviews on these topics are Wolfe [1.11]), Bron [1.12].

Non-dissipative sound attenuation in solids – i.e. sound scattering from imperfections like grain boundaries or diffraction losses from diffraction effects from the transducers or due to nonparallelicity of the crystal or due to mode conversion on the surface etc. – will only be mentioned occasionally. Also dislocation damping in all its different manifestations (point defect relaxation, Snoek relaxation, Zener relaxation, dislocation motion or eddy current effects) have been investigated in the early treatises and will not be covered in this text. See for the latter effects e.g. Nowick and Berry [1.13]).

The cgs-Gauss mass system is mostly used in this book since in the solid-state physics literature this mass system is used. Changes to the SI system or tables for units can be found in Appendix A.

An introduction to the field is given in the first three chapters. Experimental techniques are described in Chap. 2. The emphasis is especially on new developments that have not been covered in previous books on ultrasonics cited above. These new developments are e.g. resonant ultrasonic spectroscopy, ultrasonics in high pulsed magnetic fields, high resolution Brillouin scattering. Chapter 3 introduces elasticity emphasizing the symmetry aspects which are not covered in other books. Chapter 4 presents the necessary background of thermodynamics with the thermodynamic potentials and functions. The Landau theory of phase transitions and the range of its validity is also presented. The following Chaps. 5–14 cover the full range of the various applications in solid state physics.

This book is intended for all those who want to know what can be learned from ultrasonics about the solid state. I hope to give an updated account of this field. Graduate students and researchers in the field of physical acoustics or related fields, should also benefit from this book. Since the whole outlook of the book is based on Solid State Physics some books on this topic are listed for the reader: "Solid State Physics" by Ashcroft and Mermin [1.14], "Festkörperphysik" by Ibach and Lüth [1.15], "Introduction to Solid State Physics" by Kittel [1.16]. Recently a "Handbook of Elastic Properties of Solids, Liquids and Gases" (Editors: M. Levy, H.E. Bass, R.R. Stern) appeared placing emphasis on measuring methods and surveys on quite different materials (elements, novel materials, building materials). The outlook of this handbook is quite different to the one given in the present book.

2 Experimental Techniques

A discussion follows on the various experimental techniques used for ultrasonic investigations. In the last few decades, considerable progress has been made in the field of high resolution sound velocity and sound attenuation measurements. A wide variety of different methods are used in this field. A distinction can be made between techniques which use transducers and others which are contact free methods. To the latter ones belong the vibrating reed technique and the Brillouin scattering. Numerous books and review articles describe all these topics.

In the low frequency regime, where the sound wavelength is of the dimension of the specimen, the elastic moduli (Young's modulus E and shear modulus G) can be determined by a c.w. resonance method or by measuring flexural and torsional oscillations. At audio frequencies the vibrating reed technique is most frequently applied (Read et al. [2.1]). A brief account of this technique is given in Sect. 2.2.5. In the ultrasonic regime, the elastic constants c_{ij} can be determined by using pulse or c.w. techniques (Truell et al. [2.2], Bolef and Miller [2.3], Fuller et al. [2.4]). The most widely used method to measure sound velocity and attenuation is the pulse superposition technique or variations of it (Truell et al. [2.2], Fuller et al. [2.4]). A particularly interesting method is the shape resonance technique, also called resonant ultrasound spectroscopy (RUS), suitable for small crystals and low symmetry crystals (Migliori and Sarrao [2.5]). This technique will be discussed together with phase sensitive sound velocity and attenuation measurements in Sect. 2.2. In Sect. 2.3 a short account of phonon echoes will be given. In Sect. 2.4 ultrasonics in pulsed high magnetic field will be described. Apart from the low frequency and the ultrasonic regime, sound waves can also be generated in the microwave region (Tucker and Rampton [2.6]). A method which was used for various applications is the excitation of microwave sound at surfaces in microwave cavities. This will be discussed in Sect. 2.6. The excitation and detection of acoustic surface waves SAW will be discussed in Sect. 2.5. Finally, in Sect. 2.7, the Brillouin scattering will be mentioned. Thermal expansion and magneto-striction experiments are important to determine the length changes with temperature or magnetic field. Apart from this they are important thermodynamic functions in their own right. The experimental technique for these quantities and for measuring thermal conductivity will be discussed in Sect. 2.8. We begin with a discussion of ultrasonic transducers in Sect. 2.1.

2.1 Transducer

Several techniques are in use to generate and to detect ultrasonic waves. The most common one is to use piezoelectric transducers. But also magnetostrictive transducers or electromagnetic generation and detection of sound can be used in special cases. A brief review of the different techniques to generate and detect sound waves follows and some review articles where more details can be found are named.

With the strains and stresses defined in Chap. 3, the piezoelectric effect gives a stress–strain electric field relation

$$T_i = c_{ik}\varepsilon_k - e_{ij}E_j \,. \tag{2.1}$$

Here we use already the contracted Voigt notation, see Sect. 3.1 ($11 \to 1$, $22 \to 2$, $33 \to 3$, $23 \to 4$, $13 \to 5$, $12 \to 6$) for the stress tensor T_{ij} and the strain tensor ε_{ij}. c_{ij} are the elastic constants and e_{ik} the piezoelectric stress coefficients. The inverse relation reads

$$\varepsilon_i = s_{ik}T_k + d_{ij}E_j \tag{2.2}$$

with s_{ik} a component of the compliance tensor. The piezoelectric matrix in contracted notation is given by (e_{ij}) with $i = 1,2,3$ (3 directions) and $j = 1,\cdots,6$ (six components of the stress tensor). For quartz (SiO_2) it has the form

$$[e_{ij}] = \begin{pmatrix} e_{11} & -e_{11} & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -e_{14} & -2e_{14} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

with $e_{11} = 0.171C/\mathrm{m}^2$, $e_{14} = 0.0403C/\mathrm{m}^2$ with C dimension of Coulomb (Appendix A). For $LiNbO_3$ the corresponding components read:

$$[e_{ij}] = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & -e_{22} \\ -e_{22} & e_{22} & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix}$$

with $e_{15} = 3.65C/\mathrm{m}^2$, $e_{22} = 2.39C/\mathrm{m}^2$, $e_{31} = 0.31C/\mathrm{m}^2$, $e_{33} = 1.72C/\mathrm{m}^2$ (Ogi et al. [2.7]).

For an X-cut quartz an electric field in the x-direction produces a strain in the same direction, therefore producing longitudinal waves. With the parameters for quartz, the longitudinal elastic constant $c_{11} = 8.6 \times 10^{11} erg/\mathrm{cm}^3$, the piezoelectric constant $e_{11} = 0.171\frac{C}{m^2}$ and with a typical applied electric field value of $E_x = 10V/\mathrm{mm}$, the stress is given by $T_1 = e_{11}E_x = 1.71CV/m^3$ and the strain by $\varepsilon_1 = \varepsilon_{xx} = T_1/c_{11} = 0.2 \times 10^{-6}$ – a rather small strain. This would be the maximum strain for a longitudinal sound wave in the x-direction for the typical applied ac electric field. Likewise, shear waves may be generated with a Y-cut crystal. The purest shear mode with a minimum of

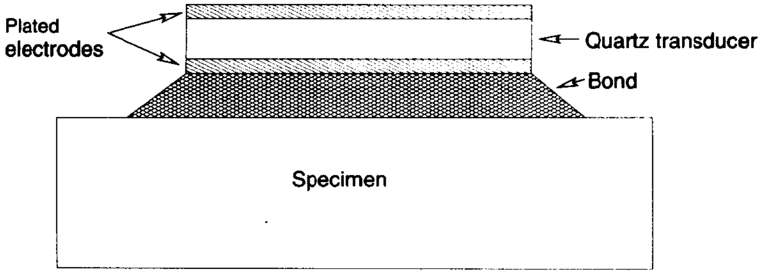

Fig. 2.1. Transducer-Bond-Specimen arrangement

coupling to other modes is the so-called AC-cut quartz crystal, a cut rotated by 31° about the x-axis.

Further details on these transducers can be found in Mason [2.8]. Another transducer material is $LiNbO_3$ with larger piezoelectric coupling constants as shown above. With these transducers, the resonance frequency or odd integer multiples thereof are used.

In addition, there are piezoelectric polymer foils with high efficiency. They can be used non-resonantly over a large frequency range. They are especially suited for longitudinal waves. All these transducers have to be bonded to the specimen with plane parallel polished faces (see Fig. 2.1). Thiokol LP, GE cement, Nonaq or UHU cement can be used as bond materials. If thin film technology is used, transducers, such as ZnO or CdS, can be evaporated or sputtered directly on to the specimen without a bond in between. Details on this fabrication technology can be found in Foster [2.9]. This thin film technique is also important for surface acoustic waves as discussed in Sect. 2.5. Problems arising with the different types of transducers for measuring ultrasonic velocity and attenuation are discussed in Sect. 2.2.

Apart from piezoelectric transducers, there have been studies also on magneto-strictive transducers and on electromagnetic generation of ultrasound. The latter ones have been carried out in metals, ferromagnets and various magnetic materials. Since these techniques have little technical application, no further details are given here but some relevant reviews are: Dobbs [2.10], Buchelnikov and Vasil'ev [2.11], Gorodetsky et al. [2.12].

2.2 Sound Velocity and Attenuation, Experimental Techniques

2.2.1 Simple Ultrasonic Set-Up

A simple ultrasonic system for producing stress waves is now discussed. In Fig. 2.1 we show the transducer–sample system. The (piezoelectric) transducer with electrodes on both sides is bonded to the specimen with parallel

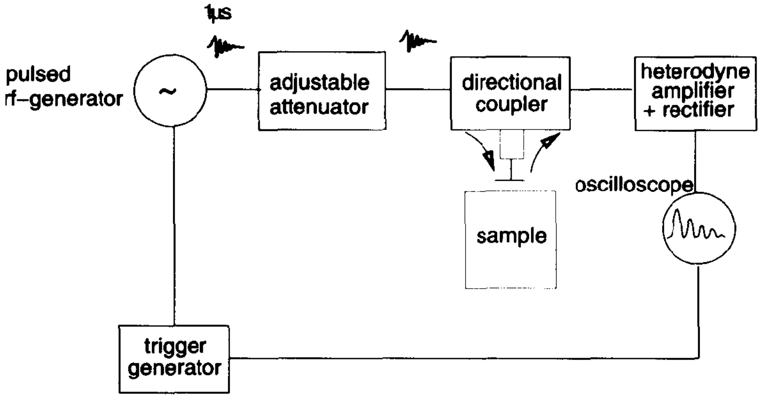

Fig. 2.2. Ultrasonic system to measure sound velocity and attenuation

end faces. For the choice of bond materials see Sect. 2.1. A pulsed electromagnetic signal of $\sim 1\,\mu s$ duration, operating at the fundamental frequency of the transducer or at one of its odd harmonics, is applied across the transducer. With the piezoelectric effect, a stress wave is produced which propagates through the specimen.

In the single transducer arrangement of Fig. 2.2, the same transducer acts as a receiver. Upon reflection on the surface, a small amount of energy is converted back to an electric pulse. The major part of the pulse is reflected and propagates further, producing an ultrasonic echo pattern as shown e.g. in Fig. 2.5a. The converted electric pulse is amplified (with homodyne or heterodyne amplifiers) and shown on the oscilloscope. To investigate a wide frequency range, transducers can be used on both opposite faces of the sample (emitter and receiver) – this does not need a directional coupler. In the following, we discuss phase sensitive devices to measure ultrasonic velocity and attenuation with high accuracy.

A distinction can be made between pulse echo techniques and cw-techniques. In the latter case, the transmitting transducer is driven continuously and a resonant response is observed at frequencies which correspond to $L = n\frac{\lambda}{2}$ with L the sample length and λ the wavelength of the sound. The ultrasonic wave velocity is determined from the resonant frequencies with transducer corrections included. The attenuation follows from the quality factor Q of the resonance signals. In the following, we discuss a special phase-sensitive ultrasonic set-up, absolute sound velocity measurements, the so-called Resonant Ultrasonic Spectroscopy (RUS) and the vibrating reed technique.