Fundamentals of Piezoelectric Sensorics

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Mechanical, Dielectric, and Thermodynamical Properties of Piezoelectric Materials

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Preface

Piezoelectricity – a direct conversion of mechanical stress to the electrical charge and vice versa – has been discovered about 130 years ago. Since that time it attracted a lot of interest from the application point of view as well as from the fundamental research as you can see in the comprehensive, although not exhaustive, list of books published during the last three decades. Piezoelectric substances are commercially produced in single-crystal form as well as in ceramics and they belong to the second biggest application of dielectric materials, just after semiconductors. Piezoelectric phenomena and their precise description require interdisciplinary theoretical knowledge of crystallography, tensor analysis, continuum mechanics, thermodynamics, non-linear phenomena as well as experimental experience with the electrical and mechanical measurements and necessary equipment. Piezoelectricity and piezoelectric materials study is a lifelong job for a researcher, like it is for authors of this book. It requires cooperation between physicists and engineers – specialists in the field. Despite of more than a hundred years of ongoing research as well as piezoelectricity application, new horizons open ahead of piezoelectricity researchers, today.

This book should be used as a theoretical foundation for the knowledge on piezoelectric sensors, excellently described by Gustav Gautschi in the book G. Gautschi: *Piezoelectric sensorics*, published by Springer Verlag in 2002. Publication of this book has been inspired by Prof. Jan Tichý about 10 years ago, who is one of the authors of the original edition of the book J. Tichý, G. Gautschi: *Piezoelektrische Messtechnik*, Springer Verlag, published together with G. Gautschi in German in 1980. The new edition of the book is extended in some chapters, translated to English and divided into two separate volumes – the first one with the physical foundations of piezoelectric sensorics, the second one mostly application-oriented piezoelectric sensorics instrumentation. The new international authors team includes Prof. Jan Tichý and his colleagues from the Technical University of Liberec, Czech Republic – namely, Prof. Jana Přívratská and Dr. Jiří Erhart – and Prof. Erwin Kittinger from the Leopold-Franzens Universität Innsbruck, Austria. Authors completed the manuscript according to his/her own specialization and interests in the field – i.e. J. Tichý prepared Chap. 1 and participated on most remaining chapters directly or through the original German text partly translated for the new edition, E. Kittinger prepared Chaps. 3, 4 and 6, J. Přívratská made Chap. 2 ready for publication and J. Erhart completed Chaps. 5, 7, Appendix and prepared the final edition of the whole manuscript.

Book content is organized in seven chapters and one Appendix. Chapter 1 is devoted to the fundamental principles of piezoelectricity and its application including related history of phenomenon discovery. A brief description of crystallography and tensor analysis needed for the piezoelectricity forms the content of Chap. 2. Covariant and contravariant formulation of tensor analysis is omitted in the new edition with respect to the old one. Chapter 3 is focused on the definition and basic properties of linear elastic properties of solids. Necessary thermodynamic description of piezoelectricity, definition of coupled field material coefficients and linear constitutive equations are discussed in Chap. 4. Piezoelectricity and its properties, tensor coefficients and their different possibilities, ferroelectricity, ferroics and physical models of it are given in Chap. 5. Chapter 6. is substantially enlarged in this new edition and it is focused especially on non-linear phenomena in electroelasticity. Chapter 7. has been also enlarged due to many new materials and their properties which appeared since the last book edition in 1980. This chapter includes lot of helpful tables with the material data for the most today's applied materials. Finally, Appendix contains material tensor tables for the electromechanical coefficients listed in matrix form for reader's easy use and convenience.

Authors are very much indebted to Springer Verlag publisher for the generosity and patience with author's problems with manuscript preparation. We also wish to thank to all our colleagues, who contributed to our work by advice, by valuable information on the new phenomena or by any specific knowledge profitable for the manuscript organization and preparation. Czech authors (J.E. and J.P.) would like to express our sincere thanks for the stimulating discussions to Prof. Jan Fousek and Prof. Václav Janovec. They stimulated our interest in piezoelectricity, ferroelectricity and related ferroic domain structure studies. Continuing support from the Grant Agency of the Czech Republic during the whole manuscript preparation is also highly acknowledged by one of the authors (J.E.). Among many projects let us name at least the last one – project No. P202/10/0616. Last but not least, J.E. would like to thank to his wife Vladimíra Erhartová for her patience and kind understanding during preparation of the manuscript.

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Chapter 1
Principles of Piezoelectricity

In the first part of this chapter we give a qualitative description of the piezoelectric effect. The material in the following sections will provide a more detailed account of the piezoelectricity. The next part is a survey of pioneering research in this field by Pierre and Jacques Curie. We mention also Lipmann's prediction of the converse effect. Finally we describe briefly some successes achieved in the area of practical applications of piezoelectricity and piezoelectric materials. This last part is just a brief sketch and not a complete picture.

1.1 The Direct and the Converse Piezoelectric Effect

Piezoelectricity is linear interaction between mechanical and electrical systems in non-centric crystals or similar structures. The direct piezoelectric effect may be defined as the change of electric polarization proportional to the strain. A material is said to be piezoelectric if the application of an external mechanical stress gives rise to dielectric displacement in this material. This displacement manifests itself as internal electric polarization. It should be noted that the piezoelectric effect strongly depends on the symmetry of the crystal. A crystal having sufficiently low symmetry produces electric polarization under the influence of external mechanical force. Crystals belonging to the 11 point groups having central symmetry are unable to produce piezoelectric effect. With one exception, all classes devoid of a centre of symmetry are piezoelectric. The single exception is the Class 29 (enantiomorphous hemihedral), which, although without a centre of symmetry, nevertheless has other symmetry elements that combine to exclude the piezoelectric property.

Closely related is the converse (reciprocal, inverse) effect, whereby a piezoelectric crystal becomes strained if an external electric field is applied. Both effects are the manifestation of the same fundamental property of the non-centric crystal. Only for historical reasons the term "direct" is used about the first and not the other effect.

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We can study piezoelectricity using quartz crystals. A plate cut at right angles to the x-axis is called X-cut. Let its thickness be small in comparison with the other dimensions. We subject this plate to a pressure parallel with the thickness. If a compressional force (size) **F** is used, the polarization P_1 parallel to the thickness is proportional to the stress $T_{11} = F/A$. Hence the piezoelectric polarization charge on electrodes covering the major faces A is proportional to the force causing the strain.

If we apply tension, the sign of pressure is reversed and the sign of the electric polarization reverses too. When an electric field **E** is applied along the thickness of the plate the quartz plate is deformed. The deformation (the strain S_{11}) changes sign when the polarity of the field is reversed (Fig. 1.1).

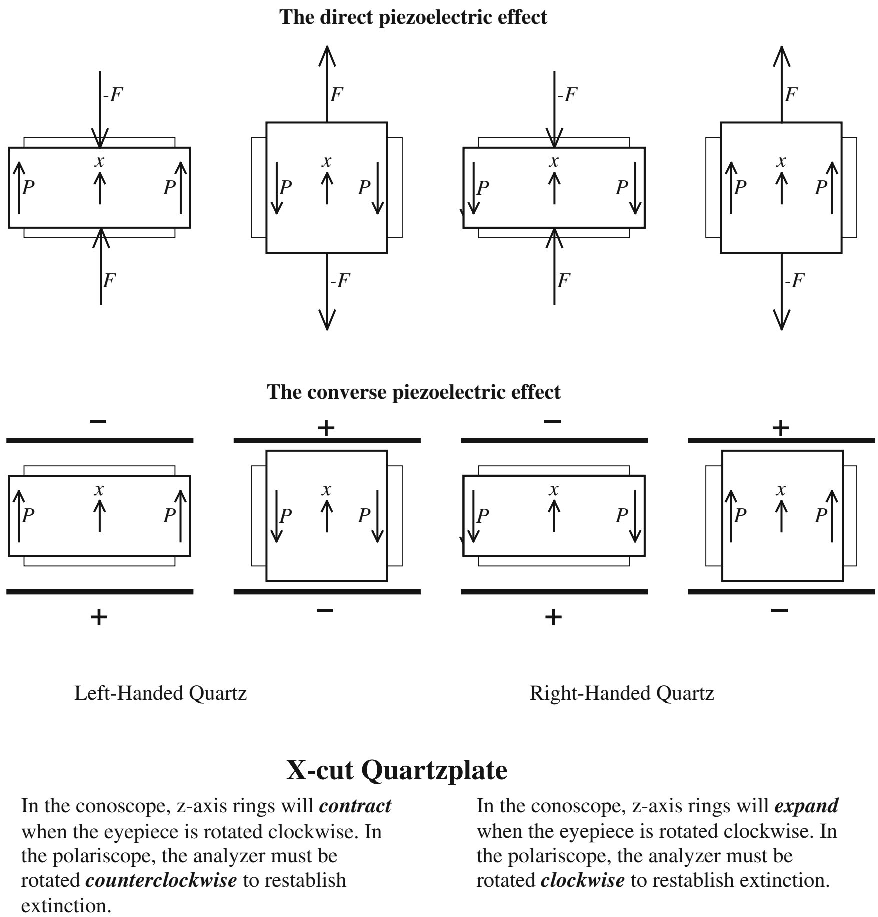

Fig. 1.1 Direct and converse piezoelectric effects

The direct piezoelectric effect is described by

$$P_1 = d_{111}T_{11}, \tag{1.1}$$

where P_1 is the component of the polarization vector and T_{11} is the component of the stress tensor. The coefficient d_{111} is called the piezoelectric coefficient. Conversely, if an external electric field E_1 is applied, a strain S_{11} is produced

$$S_{11} = d_{111}E_1. \tag{1.2}$$

The development of standards on piezoelectric crystals has been the product of considerable work and debate by many people. The existence of enantiomorphic crystal forms led to changes in sign conventions from time to time, as the standards committees tried to make the conventions easier to understand and use. We use the co-ordinate system adopted by the IEEE Standards (IEEE Standard on piezoelectricity 1987) adopted a right-handed co-ordinate system for all crystals and quartz is not considered an exception. The crystallographic –*a* axis is taken as *X* for the right quartz, whereas the +*a* axis is taken as *X* for the left quartz. Extensional stress along *X* induces a positive charge in the direction of positive *X* in the right quartz, but compressional stress produces the same result in the left quartz. The sign of the piezoelectric constant is positive when a positive charge is produced in the positive direction of the axis as a result of a positive (extensional) stress. Consequently piezoelectric coefficients are positive for right quartz, and they are negative for the left quartz.

Polarization associated with a given strain is always the same, whether the strain is due to mechanical forces (direct effect) or to an impressed electric field (converse effect). Later on, in Chap. 4, we will prove the equality of the piezoelectric constants used to describe both effects.

We will always assume that the state of the crystal is homogeneous both electrically and mechanically, which means that all volume elements are at exactly the same temperature and that the field and the strain have the same values everywhere. We further assume the linearity of equations describing the piezoelectric effect. In this case the complete solution of the problem can be found. Physicists usually treat a natural phenomenon using a simple mathematical form. It is a linear approximation. An the other hand, the MacLaurin or Taylor series are popularly used to calculate slightly perturbed physical quantities around an equilibrium state including non-linear effects. We talk about a non-linear expansion theory. However, when we have to take into account boundary conditions, the situation becomes so complicated that the only way to find the solution is the finite element method. This method is also used to find complex distribution of stresses in a piezoelectric plate compressed along the thickness by means of steel plates. Finite element methods are also used in a number of other special cases. Fortunately boundary conditions can be usually ignored. In the following chapters we are going to consider only linear systems and the variables of two different quantities will be linearly coupled.

1.2 Discovery of Piezoelectricity

The phenomenon of piezoelectricity was discovered by brothers Curie: Pierre (1859–1906) and Jacques (1855–1941). In 1880 they found (Curie and Curie 1880) that some crystals when compressed in certain directions show positive and negative charges on some portions of the surface. These charges are proportional to the pressure and disappear when the pressure ceases.

This was no chance discovery. Their approach was influenced by Pierre Curie's previous work on pyroelectricity and symmetry of crystals. He found that polar electricity is produced only along certain directions depending on the symmetries of particular crystallographic classes. Some time earlier another effect had been discovered. A change in temperature of a crystal can cause a number of electrical effects known as pyroelectricity. Pyroelectricity is the manifestation of the temperature dependence of spontaneous polarization of certain solids. These are either single crystals or polycrystalline aggregates. The piezoelectric effect is closely related to the pyroelectric effect. The connection between pyroelectricity and piezoelectricity is fundamental. All pyroelectric materials are intrinsically piezoelectric. We know now that pyroelectric materials form a subgroup of piezoelectric materials. Prefixes "piezo" and "pyro" are derived from Greek words with meanings "to press" and "fire", respectively.

If "lyngourion" and the mineral tourmaline are identical then the words written by the Greek philosopher Theophrastus some 23 centuries ago could be the earliest description of the pyroelectric effect of tourmaline. Two thousand years after Theophrastus strange properties of tourmaline became known in Europe thanks to the book of Johann Georg Schmidt in 1707 and entitled Curious Speculations during Sleepless Nights (Lang 1974).

The fact that tourmaline when placed in hot ashes at first attracts and later repels them was known for a long time. This behavior became known in Europe about 1703, when Dutch merchants brought tourmalines from Ceylon. The attractive power of this crystal seems to be well known in Ceylon and India since time immemorial. Tourmaline was sometimes called "Ceylonese magnet". The great naturalist Charles Linné (Linnaeus) was apparently the first person to relate the pyroelectric properties of tourmaline to electric phenomena. He gave it the scientific name *lapis electricus*. The first serious scientific study of the electrical properties of tourmaline was presented to the Royal Academy of Sciences in Berlin, by Franz Ulrich Theodor Aepinus, in 1756. He noticed that the two ends of a heated tourmaline have opposite polarities. David Brewster observed this effect on several kinds of crystals and in 1824 gave it the name "pyroelectricity". His paper was entitled "Observations on the Pyro-Electricity of Minerals". Brewster invented a sensitive test for pyroelectricity by placing a thin slice of material on a glass plate heated by boiling water. In 1828 A.C. Becquerel was probably the first scientist to attempt to make quantitative measurements of pyroelectricity. One of the crystals, in which he found pyroelectric effect, was Rochelle salt.

The first definitive theory of pyroelectricity, with which majority of later investigators agreed, was formulated by William Thomson (Lord Kelvin) in 1878 and

1893 (Thomson 1878). Pyroelectric crystals have a unique polar axis, which does not necessarily coincide with any direction derived from symmetries of the crystal. Lord Kelvin postulated that such crystals are in a state of permanent polarization. This theory links changes in spontaneous polarization ΔP_S with changes of temperature $\Delta\Theta$ by means of linear equation. The constant connecting these two quantities is the pyroelectric coefficient π

$$\Delta P_S = \pi\ \Delta\Theta \tag{1.3}$$

The pyroelectric effect has become simply a manifestation of the temperature dependence of spontaneous polarization.

In the nineteenth century, several researchers (e.g. Becquerel and Haüy) tried to find a connection between effects of mechanical pressure and electrical effects. Becquerel even expected that similar effects should exist specifically in crystals. The predecessors of brothers Curie produced, however, only some results of a rather dubious value. Effects attributed to piezoelectricity were often found in crystals, which, because of their symmetry, should not be piezoelectric. In some instances similar effects were found even in non-crystalline materials. These odd results could be explained by electrical charges released by friction in the instrument during the experiment.

The relation between pyroelectric phenomena and symmetry of crystals, which Pierre Curie investigated earlier, led the two brothers not only to look for electrification by pressure but also made it possible to predict in what direction the pressure should be applied and to select the classes of crystals, in which the effect was expected. We feel that it is fitting to insert here the translation of the opening paragraphs of the paper, in which they announced the discovery of the effect.

> Those crystals having one or more axes whose ends are unlike, that is to say hemihedral crystals with oblique faces, have the special physical property of giving rise to two electric poles of opposite signs at the extremities of these axes when they are subjected to a change in temperature: this is the phenomenon known under the name of pyroelectricity.
>
> We have found a new method for the development of polar electricity in these same crystals, consisting in subjecting them to variations in pressure along their hemihedral axes.

The first paper on piezoelectricity by Jacques and Pierre Curie was presented to the Société minéralogique de France at the session on the 8th of April 1880 and later to the Académie des Sciences at the session on the 24th of August 1880. Pierre and Jacques Curie at first discovered the direct piezoelectric effect in crystals of tourmaline. They noticed that as result of pressure applied along a particular direction, electrical charges proportional to the pressure and of opposite polarities appear on opposite crystal surfaces. They called this effect "polar-electricity". Later, they discovered a similar effect in quartz and other crystals, which have no centre of symmetry. At that time Pierre Curie was only 21 years old. His notes published in Comptes Rendus in 1880 and 1881 are a real gem, as they deal with all essential phenomena (surface charge is proportional to pressure and does not depend on the thickness of the crystal etc.).

Several months later Lippmann made an important contribution to piezoelectricity by predicting the converse effect on the basis of the principles of thermodynamic (Lippmann 1881). A piezoelectric crystal placed in an electric field must undergo a deformation. Brothers Curie immediately suggested a beautiful and simple experiment to detect small deformations. They coupled mechanically the investigated crystal to a second piezoelectric crystal, which played the role of a detector by converting the mechanical signal produced by the first crystal into an electric signal measured by an electrometer. The predictions of Lippmann were brilliantly confirmed (Curie and Curie 1881).

In later papers brothers Curie described piezoelectric properties of other crystals and produced the results of first quantitative measurements of the effect in quartz and in tourmaline. They suggested further laboratory experiments that could profit from the exploitation of the piezoelectric effect. In 1888 Pierre and Jacques Curie suggested that the piezoelectric quartz be used in metrology as an instrument to measure electric charges and low intensity currents. An instrument based on piezoelectric quartz played an important role in Marie Curie's later work on radioactivity.

Hankel contended that the new effect obeyed it's own special laws and proposed for it a name "piezoelectricity". His proposal was promptly accepted by all, including brothers Curie themselves (Hankel 1881).

Shortly thereafter, Pierre Curie became director of a teaching laboratory at the Ecole de physique et de chimie. The young director of physics laboratory made a remarkable decision to start in three directions at the same time, namely to teach, to develop new instruments and to engage in theoretical research.

Curie wrote about properties associated with symmetries of fields. Thanks to his excellent education in crystallography he very early understood the importance of symmetry considerations. He formulated the essential principle by realizing that the symmetry of "effect" is dependent on the symmetry of "cause". The eminent role of symmetry in the formulation of laws of physics has been more and more noticeable during the last 50 years.

In 1894 Pierre Curie started to study magnetism. At that time he had just been nominated professor. He accepted as his student to do research in magnetism a Polish lady, Marie Skłodowska. In 1895 they were married and she became Marie Curie. In 1898 the two of them began to study radioactivity. Marie Curie received the Nobel prize for chemistry in 1911 for her work on polonium and radium. Pierre Curie died by an accident in 1906. He was only 47 years old.

A polar material, whose electric dipoles can reverse direction as a consequence of an external electric field, is by definition a ferroelectric material. These materials form a subgroup of pyroelectric materials.

1.3 History of the Theory of Piezoelectricity and of Piezoelectric Materials

When studying the piezoelectric effect we can take either the macroscopic (phenomenological) approach or the microscopic (atomistic) approach. Both these views were important in the development of solid state physics.

The problem of the relation between pyroelectricity and piezoelectricity was the object of many wide-ranging discussions. This work was done mainly by Voigt. The phenomenological theory of piezoelectricity is based on the principles of thermodynamics formulated by Lord Kelvin. In 1890 Waldemar Voigt published the first complete and rigorous formulation of piezoelectricity (Voigt 1890). The formulation used in the physics of crystals today owes much to Voigt's monumental work "Lehrbuch der Kristallphysik" (Voigt 1910). Voigt formulated the theory of thermodynamic potentials for piezoelectricity.

One could argue that this phase of development in solid state physics was concluded by the publication of Voigt's famous textbook in 1910. The underlying reason is the importance of the symmetry of crystals for all other properties. However, a good understanding of the thermodynamics is of utmost importance for the solution of all problems in the physics of crystals. We could say that for a physicist further development of thermodynamics is less important than the development of microscopic models. For all technical applications, however, thermodynamics is of special importance.

The foundations of the thermodynamic theory of elastic dielectrics and of piezoelectricity were laid down by Toupin, Eringen, Hájíček, Grindlay and other researchers (Tichý and Gautschi 1980) in the second half of the twentieth century. Both experimental and theoretical research of non-linear effects in dielectrics is being continued even today (Kittinger and Tichý 1992; Nelson 1979).

In the late forties V.L. Ginzburg and A.F. Devonshire produced a phenomenological description of piezoelectric and other properties of ferroelectrics.

A thermodynamic theory explaining the behavior of ferroelectric crystals can be obtained by considering the form of the expansion of the free energy as a function of the polarization. The Landau theory and the complementary theory of critical phenomena offer the possibility of working out the universal properties of systems undergoing phase transitions on the sole basis of symmetry considerations. Some classes of structural transitions have been thoroughly investigated during the past decades, such as ferroelectric and ferroelastic transitions. Reconstructive phase transitions have been left aside from the preceding theoretical framework. They constitute the most fundamental and widespread type of structural transitions existing in nature (Tolédano and Dmitriev 1996).

The first attempt to establish an atomic theory of piezoelectricity is considered to be the work of Lord Kelvin. Using Debye's theory of electrical polarization Schrödinger attempted to determine the order of magnitude of the piezoelectric constants of tourmaline and quartz. However the first to succeed was Born in 1920 in his book "Lattice-dynamical theory". An atomic model for the qualitative explanation of piezoelectric polarization of quartz was discovered by the method of X-ray analysis by Bragg and Gibbs in 1925.

Modern atomic theory has a challenging task of shedding light not only on piezoelectric properties, but also on other physical properties of materials by means of quantum mechanics. To do this, one needs not only to understand the properties of atoms at rest in their equilibrium position, but one has to take into account the changes due to motion. The dynamic matrix theory treats the whole crystal matrix as one single quantum mechanical system.

All this, together with the recognition of the importance of symmetry for the laws of physics makes the explosion of our knowledge during the second half of this century even more impressive.

In recent years, even piezoelectric, pyroelectric, and ferroelectric effects in biological materials are the subject of investigations. Pasteur was probably the first to suggest over 100 years ago that biological systems have chiralic dissymmetric properties and that these properties are important for the functioning of the biological systems. In the 1960s it was suggested that piezoelectricity is a fundamental property of biological materials and it is observed in different soft and hard tissues: human femur, skin, Achilles tendon of ox and horse, wood and so on. Piezoelectric ceramics like PZT can be poled by the electric field, while the biological substances like wood have a unique axis generated in their growing process.

1.4 Applications of Piezoelectricity and Pyroelectricity

Practical application of piezoelectricity proceeded at an uneven pace. Periods of slow progress were followed by periods of rapid development. Practical application of piezoelectric materials was rather limited during the first third of the time elapsed since their discovery. In the "Oeuvres" Pierre and Jacques Curie describe several ingenious piezoelectric devices meant for static measurements of various parameters. Piezoelectricity makes possible the transformation of electric into acoustical signals. Using piezoelectric crystal it is possible to generate required quantities of electric charges very accurately. This is needed in the construction of precision electrometers. Such devices were used for the measurement of capacitance, voltage, pyroelectric and piezoelectric effects and in the measurements of radioactivity.

In 1917 the National Research Council sponsored a conference chaired by Robert A. Millikan. W.G. Cady was invited because of his interest in the detection of submarines by ultrasonic waves. Paul Langevin reported the generation of ultrasonic waves by means of transducers using quartz and steel sandwich. This device, called Langevin's transducer, is an original application of piezoelectricity in ultrasonic engineering. He used both direct and converse piezoelectric effects of a large quartz plate firstly to emit underwater sound waves and for their subsequent detection. This device opened the field of ultrasonic and hydroacoustics. Sonar exists thanks to the activity of Paul Langevin.

The conference persuaded Cady to turn his interest to piezoelectricity. In 1919 Cady initiated the study of resonators and the first report on piezoelectric resonator was presented to the American Physical Society in 1921. He proposed the piezoelectric quartz resonator as a frequency standard or a filter. Cady showed how to connect a resonating quartz crystal to an electrical oscillator and in this way to achieve frequency stability. Studies of properties of crystal resonator represented by its equivalent electrical circuit were undertaken by Butterworth, Dye, Van Dyke and Mason. They led to a better understanding of crystal resonators used in filters and oscillators. The next important step is connected with the development of broadcasting. Oscillators with quartz crystals were first used by the US National Bureau of Standards as frequency standards. Around 1926, a quartz oscillator was used for the first time to stabilize the frequency of a transmitter. Cady is considered to be the father of modern piezoelectricity (Cady 1964). He was born in 1874 and died on the day before his 100th birthday (Lang 1975).

Piezoelectric materials are used in resonators, watches, crystal and ceramic filters, SAW filters, delay lines, ultrasonic transducers, underwater acoustic devices, underwater microphones and speakers, fish-finders and diagnostic acoustic devices. They are also used to generate high voltage for ignition and as piezoelectric transformers. Piezoelectric transformers are devices, which utilize both direct and converse piezoelectric effect to transform resonant voltage. Further applications of piezoelectrics to sensors and actuators have been dramatically accelerated, in addition to the discovery of new materials and devices. Some of the highlights include electrostrictive materials for positioners, relaxor-type ferroelectric polymers, normal ferroelectric single crystals with very high electromechanical couplings for medical transducers, thin or thick PZT films for micro electromechanical systems starting from a sophisticated chemical technology. Multilayer type actuators are tuning forks, vibration reeds, alarm systems and systems of remote control. At the present time there is a mass production of watches and ceramic filters. They enjoy much larger market than any other piezoelectric device. Recent enthusiastic development is found in ultrasonic motors. Precision positioners and pulse drive linear motors have already been installed in precision lathe machines. The piezo-actuators and ultrasonic motors have been developed largely by private industries in Japan, aimed primarily at applications involving precision positioners and compact motors with tiny actuators of less than 1 cm.

The research field is also very wide. It stretches from the properties of piezoelectric and ferroelectric materials, their manufacture, up to measurement techniques and practical applications. As a result we can expect in the near future the development of many new commercial products for industry and military.

The common feature of all piezoelectric devices used in high frequency technology and in ultrasonics is the fact that piezoelectric components are excited to vibrate at their resonant frequency by means of the reciprocal piezoelectric effect. Together with these two areas of practical application a third area began to develop at the same time. This is the piezoelectric measurement of mechanical quantities, namely measurement of forces, pressures and acceleration. In principle the direct piezoelectric effect is used. In this kind of measurement we usually consider it important to avoid resonance effects in the piezoelectric components. Only seldom the resonance effects are used, as for example in the measurement of pressure by change in the resonance frequency of a piezoelectric resonator. Pioneering work in this area was done by several authors: Galitzin, Karcher, Keys, Thomson and Wood (Tichý and Gautschi 1980).

In recent years, piezoelectric actuators are more and more widely used in precision instrumentation, in manufacturing and in mechatronics. In this type of applications the piezoelectric materials have the disadvantage of a small displacement, which is hardly able to meet the requirements. In order to get round this obstacle, a mechanical amplifier is normally used.

Piezoelectric devices are used in the following areas: Measurement of pressure, measurement of vibrations, stress gauge, strain gauge, measurement of acceleration, impact detector, position sensors. There is a wide choice of materials and material forms that are actively piezoelectric. Most of them have the ability to convert mechanical strain into an electrical charge when used as sensor, and to do the opposite when used as an actuator. Studies of piezoelectric semiconductors, nonlinear effects and surface waves led to construction of useful devices. The research of sophisticated electroacoustic devices may one day simplify the dialogue between the user and the computer. There are many more examples of this kind one could mention.

The most important applications of pyroelectric effect are in the field of detectors of infrared radiation, thermal imaging and pyroelectric vidicons and photoferroelectric detectors. Pyroelectric materials are also used in electrically calibrated pyroelectric radiometers, for measurement of energy, in chemical analysis and in

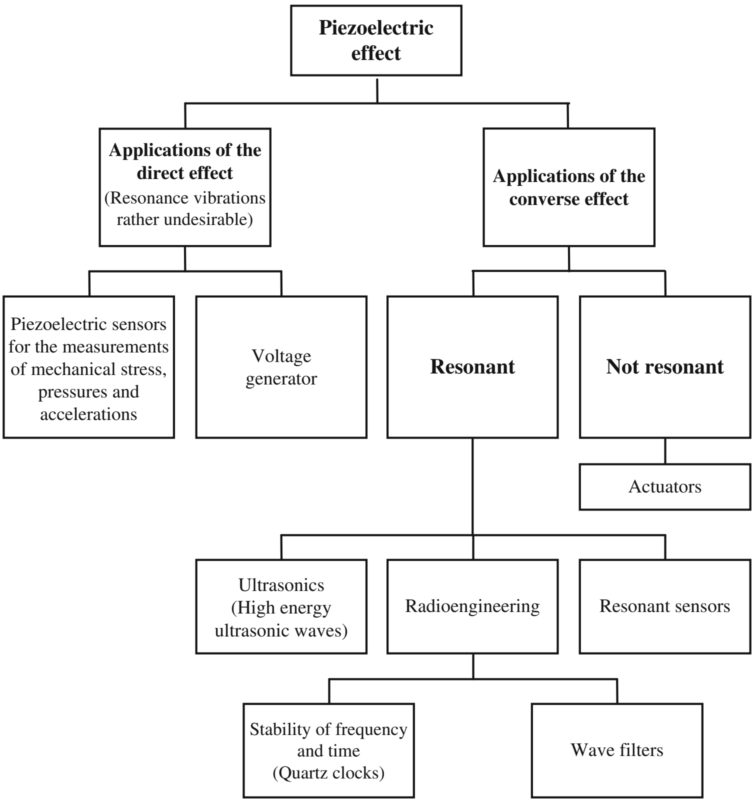

Fig. 1.2 Technical applications of piezoelectricity

biological applications. The sensitivity of pyroelectric detectors is generally limited only by the amplifier noise. The detectors have very good response in the high frequency range and can be made spectrally selective by absorptive coating on the top electrode. Figure 1.2 gives a summarized outline of technical applications of piezoelectricity.

Ferroelectric materials, especially polycrystalline ceramics, are utilized in various devices such as high-permittivity dielectrics, ferroelectric memories, pyroelectric sensors, piezoelectric transducers, electrooptic devices, and PTC (positive temperature coefficient of resistivity) components.

1.5 New Piezoelectric Materials

One hundred years have passed since Pierre and Jacques Curie discovered the piezoelectric properties of quartz. During these years study of crystals and application of piezoelectricity made a huge progress. Quartz remains still one of the most important piezoelectric materials and is in great demand. A large part of this demand is increasingly being met by mass production of artificial quartz based on the technique of hydrothermal growth.

During World War II., about 75 million quartz plates were produced for the armed forces of the United States. As the supply of good quality raw material started to decline, interest in artificial growth was renewed. The size of synthetic crystals increased tenfold thanks to the concentrated effort and modern technology. As a result, we now have a virtually unlimited supply of untwinned specimens large enough to satisfy all foreseeable needs. The quality of these crystals is more uniform than that of natural crystals. Synthetic quartz has been commercially available since 1958. Today, the manufacture of synthetic quartz has become an important industry.

J. Valasek (1920, 1921, 1922, 1924) discovered the ferroelectric effect of a single crystal in about 1921. Jaffe, who went to the United States in 1935, assisted Cady in the study of Rochelle salt. Rochelle salt was often used in various transducers because it has a great piezoelectric effect. In spite of being a piezoelectric crystal with the highest electromechanical coupling coefficient, Rochelle salt is of limited use because it is soluble in water, deliquescent and some parameters do not have a suitable temperature characteristic.

Since 1935 attempts were made to produce piezoelectric crystals, which could replace quartz. Piezoelectric crystals such as ammonium and potassium salts ($NH_4H_2PO_4$ – ADP, KH_2PO_4 – KDP), ethylene diamine tartrate (EDT), dipotassium tartrate (DKT) and lithium sulphate monohydrate (LH) were developed. Most noteworthy was the activity of the group of Bell Telephone Laboratories headed by Warren P. Mason (1964). Many of these materials are no longer in use as a result of development and production of artificial quartz, ferroelectric crystals or piezoelectric ceramics. The discovery of the strong piezoelectric properties of ferroelectric ceramics is a major milestone in applications of piezoelectricity.