PIEZOELECTRICITY

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Photograph of Jacques (left) and Pierre (right) Curie. This picture was taken in the garden of their parents in Fontenay aux Roses at the time of the discovery of piezoelectricity.

Photograph courtesy of Madame S. Zak Lehrer, Director of Publications Editions du Mont-Fermeil, Paris, France.

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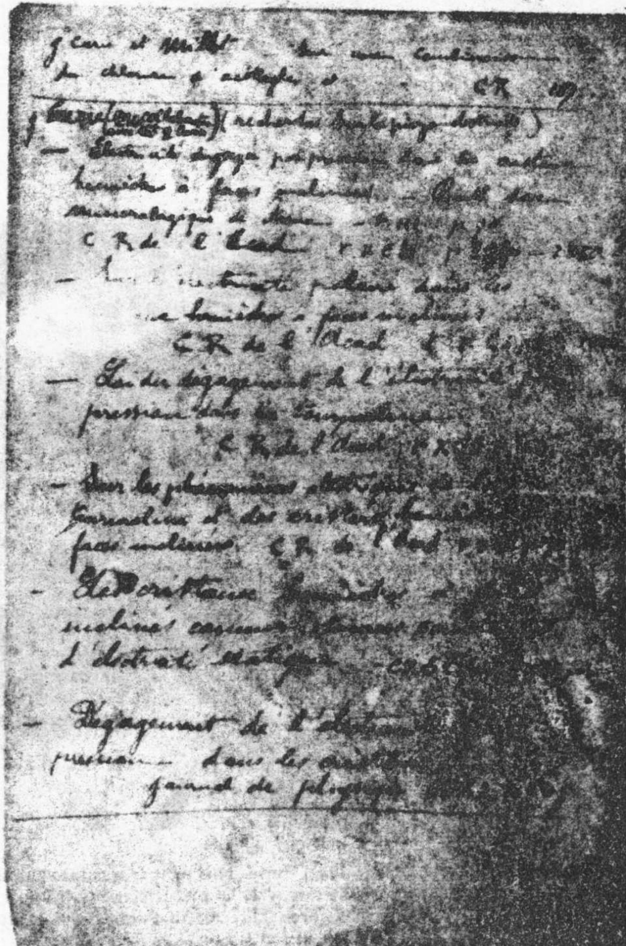

Premiers travaux de Jacques Curie

1876 1882

Document Daniel Curie – Archives ESPCI

Photo SNC

Original list of publications written by the hand of Jacques Curie, corresponding to his works between 1876 and 1882. In this list appear the earlier works on piezoelectricity.

This list was made by Jacques Curie when he applied for a position at the University of Montpellier, France.

Photograph courtesy of Madame S. Zak Lehrer, Director of Publications Editions du Mont-Fermeil, Paris, France.

PREFACE

In 1979, Professor Koichi Toyoda of the Research Institute of Electronics, Shizuoka University, Japan, suggested to one of the editors (GWT) that a special issue of the international journal *Ferroelectrics* be published to commemorate the 100th anniversary of the discovery of the piezoelectric effect. Guest editors were subsequently selected from France, Japan, the USA, and the USSR. The result was a special issue of *Ferroelectrics* (Volumes 40, No. 3/4 to 43, No. 1/2) containing sixty-eight papers from leading specialists in piezoelectricity from universities, research institutes, and industrial laboratories all over the world.

The international scientific community responded most favorably to this special issue. Many colleagues subsequently suggested that a book based on the special issue of *Ferroelectrics* would be of particular value to individual scientists and engineers who are working with piezoelectricity or who wish to become acquainted with the most recent developments in the field. This book is a result of those suggestions. The material contained is a balanced mixture of review articles, invited papers, and reports on original work covering both basic research in and applications of piezoelectricity.

In order to limit this book to a reasonable size we were obliged to choose only thirty of the original sixty-eight papers for inclusion. As is invariably the case in such matters, the choice became painful and somewhat subjective. The general criterion applied in deciding which papers to include was that they would illustrate both the breadth and the depth of the present-day science and technology of piezoelectricity.

It is our hope that this book will give a useful picture of the current status and future trends of the science and applications of piezoelectricity. In addition, we hope that this book will encourage further work in this exciting field.

We would like to express our gratitude to the authors of the papers contained in this book for their cooperation and support. The high quality of the papers is a reflection of the expertise of their authors. We are fortunate to number many of the authors amongst our colleagues. Finally, we would like to thank Dr. Y. Furahata of Hitachi Central Laboratory, Japan and Dr. N. M. Schagina of the Institute of Crystallography of the USSR Academy of Sciences for their valuable editorial assistance.

The Editors

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SERIES EDITOR'S INTRODUCTION

The connection between ferroelectricity and piezoelectricity is basic. All ferroelectric materials are intrinsically piezoelectric. Thus, a book on piezoelectricity is a very suitable, if not overdue, addition to this Series.

My fellow Editors, Dr. Jacques Gagnepain, Dr. Thrygve Meeker, Professor Terutaro Nakamura, and Professor Lev Shuvalov, are authorities in the science and technology of piezoelectricity who have been recognized both in their own countries and internationally. They have collected for this book a fascinating group of thirty papers written by specialists from twelve countries. The papers cover all aspects of piezoelectricity, from fundamental research to the latest applications.

I believe that this book will provide a valuable reference source for research in piezoelectricity. Also, this book should serve to introduce other scientists and engineers to the intriguing physics of piezoelectricity and to the exciting devices and systems that use the piezoelectric effect.

George W. Taylor

SECTION I

GENERAL

INTRODUCTION

The phenomenon of piezoelectricity was discovered just over a hundred years ago by the Curie brothers, Pierre and Jaques. The science of piezoelectricity has proceeded at an uneven pace in these one hundred years. Periods of rapid progress have been followed by periods of slow development and sometimes even by periods of no development (incidentally, this is characteristic of all branches of science). Every time that piezoelectricity has appeared to be exhausted as a science, the discovery of new piezoelectric effects or new piezoelectric materials initiated a new stage of rapid development and opened up new areas for the application of piezoelecricity. Piezoelectricity is currently enjoying a great resurgence in both fundamental research and technical applications.

Piezoelectricity is one of the basic properties of crystals, ceramics, polymers and liquid crystals. There are several ways to describe the piezoelectric effect. Perhaps the most common definition is that a material is piezoelectric if the application of an external mechanical stress causes the development of an internal dielectric displacement. This displacement is manifested as an internal electric polarization or a surface electric charge. Because of the way in which the elastic stress and dielectric displacement transform during coordinate axis rotation, the piezoelectric constants describing the linear relationship form a third order tensor. A simplified mathematical formulation of the piezoelectric effect is given below. More detailed treatments of the piezoelectric effect and converse effect can be found in texts[1-3].

It should be noted that the piezoelectric effect is strongly linked to the crystal symmetry. All crystals are arranged into 32 point groups. Crystals belonging to the 11 centrosymmetric point groups (i.e. S_2, C_{2h}, C_{4h}, S_6, C_{6h}, T_h, D_{2h}, D_{4h}, D_{3d}, D_{6h}, and O_h) cannot show a piezoelectric effect. Crystals belonging to the non-centrosymmetric point group O also do not exhibit a piezoelectric effect. Nearly all other nonmetallic crystals belonging to the remaining 20 point groups exhibit a piezoelectric effect of some magnitude, although some of the effects are very small.

The piezoelectric phenomenon can be described as

$$P_i = P_i^0 + {}_{jk}\Sigma d_{ijk}\, T_{jk} \qquad (1)$$

where P_i is a component of the polarization vector, P_i^0 is the spontaneous polarization and T_{jk} is a stress tensor component. The coefficients d_{ijk} are called the piezoelectric coefficient, and are third rank tensor components.

On the other hand, if an external electric field E is applied, the piezoelectric effect induces a strain:

$$S_{sj} = S_{jk}^0 + {}_i\Sigma d_{ijk} E_i \qquad (2)$$

Here S_{jk} is a strain tensor component and S_{jk}^0 is called the spontaneous strain. The relation (2) describes the converse piezoelectric phenomenon. Note that the same coefficient d_{ijk} enters both (1) and (2).

Although the piezoelectric coefficient d_{ijk} is a third rank tensor component, the last two suffixes jk denote six components of the second-rank tensor. Couples of indices,

11 12 33 23 31 12

can be written as 1 2 3 4 5 6

permitting the matrix expression of the piezoelectric coefficients to be given by

$$\begin{matrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{matrix}$$

Generally, both T_{jk} (or T_m, $m = 1, 2, \ldots 6$) and E_l are simultaneously applied to a crystal; thus we have

$$\begin{aligned} P_i &= P_i^0 + \sum_l \bar{\bar{X}}_{il} E_l + \sum_m d_{im}\, T_m, \\ S_m &= S_m^0 + \sum_l d_{lm} E_l + \sum_j \bar{\bar{s}}_{mj} T_j. \end{aligned} \qquad (3)$$

Here, X_{11} is the susceptibility second-rank tensor component, and $\bar{s}_{mj}$ is the elastic stiffness component. The elastic stiffnesses form a fourth-rank tensor, but are also abbreviated in the matrix notation. Relation (3) can be expressed in different ways, such as

$$T = c^D S + hD$$

$$E = -hS + \beta^s D$$

where c^D is the elastic compliance at constant electric flux, and β^s denotes the impermittivity at constant strain (clamped impermittivity).

In 1879 Pierre and Jacques Curie began their original studies of piezoelectricity. They conclusively demonstrated that electric charges, positive and negative, can be developed on certain parts of the surfaces of some crystals when they are compressed. Production of electric effects by pressure had been previously conjectured by antoine Becquerel[4] in 1820. The Curie brothers' approach to the effect was largely influenced by Pierre Curie's previous works on pyroelectricity and crystal symmetry which showed that polar electricity can be developed only in particular directions as a function of the symmetry properties of particular crystallographic classes. The experiments were performed on crystal slabs of blende, sodium chlorate, boracite, tourmaline, quartz, calamine, topaz, tartaric acid, sugar and Rochelle salt. The experiments used tin foil electrodes and a Thomson electrometer.

The first papers on piezoelectricity[5] by Jacques and Pierre Curie were presented at the Meeting of the Societe Mineralogique de France on 8 April 1880 and at the Academie des Sciences during the Meeting of 24 August 1880.

One year after the discovery of the direct effect, the converse effect was discussed by Lippmann[6], who proposed that on the basis of thermodynamic principles, converse effects must exist for piezoelectricity, pyroelectricity, etc. Subsequently, the converse piezoelectric effect was experimentally verified by the Curie brothers.

Then other papers by Jacques and Pierre Curie[7-12] reported a series of results from experiments on quartz and tourmaline and suggested some laboratory experiments that could use the piezoelectric effect for measuring forces or pessures and high voltages by means of a "manomètre à quartz" and an "electromètre a quartz." The most famous device was the "quartz piezoelectrique" utilized to produce known electric charges for the measurement of voltages, currents, capacitances, etc. This piezo-quartz instrument played an important role in Marie Curie's later work on radioactivity[13].

These events and publications were the beginning of the history of piezoelectricity.

It should be remembered that during the period 1879 to 1934 the Curie family contributed greatly to other areas of scientific research besides piezoelectricity. Elementary physics textbooks[14,15] and encyclopedias[16,17] emphasize the many contributions of this family (Pierre Curie, his wife Marie Sklodowska Curie, and their daughter Irene Curie, with her husband Frederick Joliot) to studies of radioactivity in pitchblende and to the discovery of radium and polonium. Marie Curie shared the 1903 Nobel physics prize with Pierre Curie and Henri Becquerel and received the 1911 Nobel chemistry prize for her work on polonium and radium.

Besides his work on radioactivity, Pierre Curie experimentally investigated the magnetic properties of many materials. He observed that the temperature of coefficients of the magnetic susceptibilities of ferromagnetic materials are all very similar. This emperical observation of the similarity of dependence of magnetism on temperature was later called the Curie-Weiss law. The Curie-Weiss law includes the idea of a critical temperature, which was later called the Curie temperature. A corresponding critical temperature for the dielectric constant is also called the Curie temperature or Curie point.

Some of the other important events and publications on piezoelectricity are as follows. In 1890 Woldemar Voigt published the first complete and rigorous formulation of piezoelectricity.[18]

In 1917 Langevin[19] applied the converse and direct piezoelectric effects to the emission and detection of underwater sound waves by means of large size quartz plates, and thus opened the field of untrasoncis and hydroacoustics.

The observation of the properties of piezocrystals (Rochelle-salt for instance) driven at frequencis near their mechanical resonances led to the development of piezoelectric resonators. A. Nicholson[20] in 1918 and W. Cady[21] in 1919 were the pioneers in this field.

Thw study of resonators began with Cady's work, and the first piezo-resonator was reported in 1921.

Cady demonstrated how a resonating quartz crystal could be associated with an electrical oscillator and how the frequency could be stabilized. At the same time, studies of the crystal resonator in terms of mechanical parameters and electrical equivalent circuits by Butterworth[22] (1915), Van Dyke[23] (1925), Dye[24] (1926), and Mason[25] (1943) led to a better understanding of how to use crystal resonators in filters and oscillators. Though it came later, the development of crystal resonators influenced the development of electronics. Vacuum tube electronics were first utilized in telephone circuits at the beginning of World War I, and in radiocommunication equipment at the end of that war. The next important step was the development of broadcasting. Quartz crystal oscillators 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. This was the beginning of its important development, which quickly spread to other applications such as aircraft communications, radio transmitters and civil communications, etc.

Several important milestones should be pointed out in the history of quartz crystal resonators. W. A. Marrison[26] of Bell Labs found in 1927 that a quartz crystal can be temperature compensated. This preliminary result was extended in 1934 by F. R. Lack, G. W. Willard, and I. E. Fair[27] with the discovery of the AT and BT cuts; still used today throughout the world. The superior temperature characteristics of the AT and BT had been found independently by I. Koga and N. Takagi in 1933[28]. Then came a large variety of crystallographic cuts, CT and DT due to S. C. Hight and G. W. Willard[29], ET and FT due to S. C. Hight[30], and GT due to W. Mason[31]. Important contributions were the development of coated crystals by Sykes, Warner and others[32]; techniques which still are widely used today. More recent improvements involve doubly rotated cuts, particularly the SC-cut (Eernisse[33]) and BVA resonator (Besson[34]).

Over the years, a very large amount of research has been done into the development of piezoelectric materials. Around 1921, J. Valasek[35] discovered the ferroelectric effect in single crystal, piezoelectric Rochelle salt. Of the original piezoelectric materials identified at the end of the last century, only quartz is still widely used and investigated.

The studies of new piezoelectric materials received a major impetus at the time of World War II. *Ammonium dihydrogen phosphate* (ADP) was found to be more suitable than Rochelle salt for submarine acoustics. At this time, A. V. Shubnikov predicted that piezoelectric properties would be found in amorphous and polycrystalline materials. His prediction was convincingly confirmed by independent, but parallel research around 1946 by S. Roberts[36], A.Von Hippel[37], B. Wul[38], A. Rzhanov[39], T. Ogawa[40] and after by many others, who found that ferroelectric ceramics of *barium titanate* and *other perovskites* (Smolensky[41]) were strongly piezoelectric. These discoveries created a boom in research into the piezoelectric properties of ceramic ferroelectrics and their application in a wide range of devices and systems.[42] Phenomenological descriptions of piezoelectric and other properties of ferroelectrics were developed in the late 1940's by V. L. Ginzburg[43] and A. F. Devenshire.[44]

In the early 1950's the very important discovery was made by Jaffe et al.[45] that solid solutions of lead zirconate titanate (PZT) have strong piezoelectric properties. The PZT ceramics and a great variety of related and modified ceramics[45] have played and continue to play a very important role in piezoelectric applications.[42] It should be noted that the discovery of antiferroelectricity in $PbZrO_3$ by Y. Takagi et al.[47] and the obtaining of the phase diagram of $PbZrO_3 - PbTiO_3$ by E. Sawaguchi[48] were critical milestones in the understanding of how to synthesize piezoelectric ceramics.

In the 1960's a need appeared for single crystals with higher piezoelectric coupling. This resulted in the development of lithium tantalate and lithium niobate. More recently there has been considerable research on the synthesis of berlinite (aluminum phosphate) which could, in principle, combine some of the useful characteristics of quartz with a high coupling factor.

Piezoelectric materials that are currently receiving much scientific attention include piezoelectric semiconductors, such as gallium arsenide, which have a wide range of interesting properties. An exciting goal with these materials is to integrate the piezo device and the semiconductor components on the same substrate. The last decade has witnessed an explosive expansion in research on surface acoustic waves. Most recently, the research has concentrated on layered systems containing piezoelectrics. Another important application of surface acoustic waves has been the development of miniature high frequency "bulk structure" filters using lithium niobate and lithium tantalate crystals for use in consumer electronic applications. Research into "bulk structure" surface acoustic wave resonators is currently a very active area. Piezoelectric polymers, thin films and composites are becoming increasingly important. This is evidenced by a series of recent international conferences devoted to PVF_2 and other piezoelectric polymers[49].

Since piezoelectricity was first discovered, the applications of piezoelectric materials have mushroomed[42]. Langevin's work opened the large field of ultrasonics, which now includes detection, nondestructive evaluation, acoustoelectricity, acoustooptics, imaging, signal processing, physical acoustics, medical acoustics, etc.

Early works by Cady and Nicolson led to frequency control, including resonators, oscillators and filters. This field initially utilized low frequencies (about 100 kHz). As time progressed, higher frequencies were needed and used. The majority of the presently mass produced high frequency piezoelectric filters are based on the Onoe theory of the multimode resonator[50]. It should be noted that the Onoe theory was inspired by Schockley's theory of energy traps[51].

Today, piezoelectric devices are found in television sets, radios, wrist watches, small computer games, automobiles, etc. Many communications and navigation systems use large numbers of very precise piezoelectric resonators for frequency control, generation and selection.

It can be observed that even with quartz, the "original" piezoelectric material, the rate of improvement of the properties of these devices is still in an accelerating phase. For instance, the stability of quartz frequency sources has improved by an order of magnitude every five or six years.

This brief historical survey does not pretend to be exhaustive. Many important works and applications are not mentioned. The field of piezoelectricity which goes from hertz to the gigahertz, from the cheapest wrist watch to the most sophisticated frequency standard, from the lighter to elaborate sensors is only partly covered in this book.

As noted in the Preface, the thirty papers that comprise this book were chosen from a larger collection of papers that are contained in a special issue of the international journal Ferroelectrics[52] published to commemorate the centenary of the discovery of piezoelectricity by Pierre and Jacques Curie. The papers included in this book were selected so as to provide a comprehensive picture of the current status and future trends of the science and applications of piezoelectricity throughout the world.

The first paper, by P. G. DeGennes, puts into historical perspective the discovery of piezoelectricity by Pierre Curie and the significance of symmetry in our understanding of the effect.

The next two papers deal with two very important aspects of piezoelectricity. The transition from the Piezoelectric paraelectric phase to a ferroelastic phase is described by A. Sawada and T. Nakamura. Relaxation in piezoelectric materials is covered in the paper by G. Arit.

The next three papers discuss three of the major applications of piezoelectricity. They are: mechanical filters, by H. Thomann and W. Wersing; electronic watches, by E. Momosaki and S. Kogure; and very high frequency oscillators, by L. Bidart.

These papers are followed by a series of papers covering some of the various nonlinear piezoelectric effects and their applications. Topics include: piezoelectric resonators in dc fields, by K. S. Alexsandrov et al.; elastoelectric effects, by S. I. Chizhikov et al.; electromechanical resonances for investigating dielectric properties, by H. Beige and G. Schmidt; electromechanical resonances for investigating structural phase transitions, by G. Sorge et al.; and elastic waves in crystals under a bias, by B. K. Sinha.

In the last decade, there has been a tremendous amount of research on piezoelectric ceramic composites and piezoelectric polymers. This work has already resulted in the development of many new industrial, military and commercial products and is expected to lead to many more applications in the near future. A series of papers representative of these exciting new areas are also included. The first of these by K. Okazaki reviews development in the fabrication of piezoelectric ceramics. K. Uchino and the late S. Nomura have written a paper on the commercially important PMN ceramics, and K. Nagatsuma et al. describe their work on the elastic properties of $PbTiO_3$ ceramics. The pioneer work on piezoelectric composites at Pennsylvania State University is represented by three papers; Piezoelectric 3-3 composites by K. Rittenmyer et al., Perforated PZT Polymer Composites by A. Safari et al. and SbSI — Polymer Composites by A. S. Bhalla et al. T. T. Wang reports on the effect of γ irradiation on the piezoelectric properties of the polymer PVF_2. Piezoelectricity in polymers is a fast growing and very important area of research. The interested reader is referred to several special issues of Ferroelectrics devoted to the subject[44]. In his paper, W. S. Williams reviews the piezoelectric effects that have been reported in biological materials.

All ferroelectric materials are piezoelectric and it is no coincidence that many of the most interesting and useful piezoelectric materials are ferroelectric. The piezoelectric measurements on the ferroelectric Ni-I Boracitie, by J-P Rivera and H. Schmid are reported.

Piezoelectric materials have always played a very significant role in acoustics. In recent times, they have found wide spread application as generators, transmitters and detectors of surface acoustic waves. V. V. Lemanov and Yu. V. Ilisavsky review the relationship between piezoelectricity and acoustoelectronics. M. Planat and D. Hauden describe the nonlinear properties of bulk and surface acoustic waves in piezoelectric crystals. G. G. Kessenikh and L. A. Shuvalov report on some particular types of transverse surface waves. J. Henaff et al. review surface acoustic waves in seven different piezoelectric crystals and T. Shiosaki and A. Kawabata report on the use of piezoelectric thin films for surface acoustic wave applications.

As noted earlier, single crystal quartz, from the time it was discovered to be a piezoelectric by the Curie brothers up until the present, has continued to be one of the most useful of piezoelectric materials. Its most widespread application is as a linear resonator. It is therefore appropriate that the last five papers that comprise this book should be devoted to quartz and its piezoelectric applications as linear resonators. These papers include an analysis of the depolarizing field effect in piezoelectric resonators by T. Ikeda and a description of some subtle effects in high-stability quartz resonators by A. Ballato et al. The effects of environmental conditions on long term frequency variations of quartz crystal units are reported on by M. I. Jaroslavsky and V. D. Lavrentsov. This is followed by a review of recent developments and future trends in quartz crystal resonators and oscillators by R. J. Besson et al. The book concludes with a paper by G. Dolino and J. P. Bachhelmer on how the mechanical properties of quartz are influenced by the α-β transition in the crystal.

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