Piezoelectric Crystals and Their Application to Ultrasonics

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PREFACE

During the past thirty years Bell Laboratories has carried out a considerable program of research and development of piezoelectric crystals and their application to such communication equipment as filters, oscillators and electromechanical transducers. Starting with the work of Nicolson on rochelle salt in 1918, continuous effort has been carried on in investigating quartz, rochelle salt and a large number of water soluble synthetic piezoelectric crystals. This work has recently culminated in the discovery of two monoclinic crystals, dipotassium tartrate (DKT) and ethylene diamine tartrate (EDT) which have such favorable properties that they are replacing quartz crystals in telephone filters, the largest application of piezoelectric crystals in the telephone system. Coming at a time when quartz in large sizes was becoming increasingly difficult to obtain, they have made possible the continuation and large expansion of the high-frequency carrier systemswhich carry a large share of the long-distance conversations.

It is the primary purpose of this book to describe this work, particularly from the experimental and theoretical side, since the developmental phases of the quartz work have already been described in the book "Quartz Crystals for Electrical Circuits." In order to make the work intelligible, chapters have been included on crystallographic systems, stresses, strains, thermal and electric relations, as well as an appendix showing how tensors can be applied to calculating the properties of rotated systems. Hence the book can be regarded as an introduction to the study of piezoelectricity. However, no attempt has been made to introduce the subject from a historical point of view. Indeed such a development is unnecessary since Cady's monumental work "Piezoelectricity," which appeared in 1946, covers such a development very completely. The emphasis has been rather on the new subjects that have appeared since that time. These include the new crystals, ammonium dihydrogen phosphate (ADP), which was used very extensively during the war as an electromechanical transducing element in underwater sound work, potassium dihydrogen phosphate (KDP), a new ferroelectric type of crystal, DKT and EDT mentioned previously and the ceramic barium titanate which produces an electrostrictive effect comparable with the largest piezoelectric effect in any crystal. On the theoretical side a new theory of ferroelectricity in rochelle salt, KDP and barium titanate, which has been developed by the writer, is more completely presented here than in any other place.

PREFACE

Piezoelectric crystals supply the electromechanical transducing element that makes possible another experimental science, ultrasonics. By means of the longitudinal and shear waves set up in gases, liquids and solids, considerable information can be obtained about the properties and molecular processes existing in these forms of matter. The last three chapters of the book are devoted to a description of the methods of producing and measuring such waves and to a description of the knowledge obtained from such measurements.

The author wishes to acknowledge many helpful comments and suggestions received from his associates at Bell Laboratories. On the theoretical side parts of the book have been read by Drs. J. Bardeen, C. Kittel and J. M. Richardson. Many suggestions for improvement in the order and readability of various sections have been received from W. L. Bond, G. C. Danielson, S. O. Morgan, L. C. Peterson, R. A. Sykes, G. W. Willard, and Mrs. E. A. Wood. In particular, Sykes, who is head of the apparatus department dealing with the application of piezoelectric crystals, has suggested a chapter ordering system which has improved the readability of the book. The writer wishes also to thank the members of the out-of-hours class who listened to a presentation of a preliminary form of the book and who contributed to the elimination of errors and the more obscure parts of the book.

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LIST OF SYMBOLS EMPLOYED

a, b, c = crystallographic axes
a_{ij} = direction cosines
A = free energy, ferroelectric constant for symmetrical bond
ΔA = free energy barrier
A' = ferroelectric constant for assymmetrical bond
$A + jB$ = attenuation and phase shift
A_λ = attenuation per wave length
A_∞ = attenuation at an infinite frequency
C = capacitance, compliance
C_s = shear compliance
C_p = specific heat at constant pressure or stress
C_v = specific heat at constant volume or strain
C_{vi} = specific heat of vibrational modes at constant volume
c_{ij} = elastic stiffness constants
C, S, V, D, T, O = Schönflies symbols
d_{ij} = piezoelectric constants relating strain to electric field
d_0 = tangential displacement
D = electric displacement, heat diffusion constant
e = electronic charge
e_{ij} = piezoelectric constants relating stress to electric field
E = electric field
f = frequency, Δf = change in frequency
f_c = relaxation frequency
f_A = antiresonant frequency
f_R = resonant frequency
F = force, internal field
g_{ij} = piezoelectric constant relating open circuit voltage to stress
G = Gibbs potential function
h = Planck's constant
h_{ij} = piezoelectric constants relating open circuit voltage to strain
h, k, i, l = Miller and Bravais-Miller symbols
i = current
I = moment of inertia
$j = \sqrt{-1}$

LIST OF SYMBOLS EMPLOYED

J_0, J_1 = Bessel's functions
k = coefficient of electromechanical coupling, Boltzmann's constant
k_i = reaction rate constant
K = heat conductivity
l = length, l_w = width, l_t = thickness
l, m, n = direction cosines
L = inductance
m = root of flexure equation
M = molecular volume, molecular weight, figure of merit of crystal
M_l = mass current tensor
n = number, order of overtone
N = number of molecules per cubic centimeter
N_A = Avogadro's number = 6.06×10^{23}
o = index number
O_{ijk} = electrooptic tensor
p = pressure
p_0 = static pressure
p_i, q_i = pyroelectric constants
P = electric polarization
P_d = dipole polarization
P_s = spontaneous polarization
PI = performance index of crystal
Q = charge per unit area, ratio of reactance to resistance, heat energy
Q_{ijkl} = electrostrictive tensor
r = ratio of capacities, radius
R = electrical or mechanical resistance, gas constant per mole
R_g, R_p = grid and plate resistance of vacuum tube
R_M = mechanical resistance per square centimeter
s_{ij} or s_{ijkl} = elastic compliance constants
S = area
S_{ij} = strain tensor
S_i = strain matrix
t = time
T = absolute temperature, taper constant
T_0 = Curie temperature
T_{sij}, T_{cij} = temperature coefficients of elastic constants
T_f = temperature coefficient of frequency
T_{ij} = stress tensor

LIST OF SYMBOLS EMPLOYED

T_i = stress matrix
u = displacement
U = internal energy
ΔU = activation energy barrier
v = velocity of propagation
v_d = dilational velocity
v_s = shear velocity
v_0 = velocity at zero frequencies
v_∞ = velocity at infinite frequency
V = electric potential
W = energy per square centimeter, activation energy barrier
x, y, z = rectangular axes
dx, dy, dz = distances along the axes
X = electrical or mechanical reactance
X_M = mechanical reactance per square centimeter
Y = admittance
Y_0 = Young's modulus
Z = electrical and mechanical impedance
Z_d = impedance of dipole arm
Z_0 = image impedance
Z_R = reflector impedance
$1, \bar{1}, m, n/m$ = Hermann-Mauguin symbols
α = temperature expansion coefficient
α_{ij} = transition probability
β = dielectric impermeability, Lorentz factor, complex factor in feedback path
β^I = isothermal compressibility
γ = ratio of specific heat, polarizability per unit volume
δ_i = $D_i/4\pi$ = electric displacement divided by 4π
δ = distance separating potential wells or molecules
Δ = determinant, half of dissymmetry between two potential wells
$\Delta^{m,n}$ = minor of determinant
ϵ = dielectric constant
κ = bulk modulus; $\Delta\kappa$ = change in bulk modulus
κ_1 = difference between high-frequency and low-frequency compressibility
λ = temperature stress constant, Lamé elastic constant
λ_s = acoustic wave length
λ_l = light wave length
λ' = hysteresis constant
Γ = reaction rate constant, propagation constant

LIST OF SYMBOLS EMPLOYED

μ = dipole moment, shear elastic constant
η = shear viscosity
η_l = enhanced solvent viscosity
η_M = molecular viscosity
ξ, η, ζ = displacements along x, y, and z axes
φ = transformation ratio
χ = compressional viscosity
ν = frequency
ρ = density
ρ_c = density of crystal
σ = entropy, Poisson's ratio
σ_n = ratio of currents
θ, φ, ψ = angles
Θ = absolute temperature
τ = relaxation time
ω = angular rotation, 2π times the frequency
ω_R = 2π times resonant frequency
ω_A = 2π times antiresonant frequency

CONTENTS

CHAPTER I

INTRODUCTION

1.1 *Nature of Piezoelectric Effect*

A plate cut from a piezoelectric crystal with electrodes attached serves not only as a capacitor for storing electrical energy but also as a motor for turning electrical into mechanical energy and as a generator for turning mechanical energy into electrical energy. Piezo is derived from a Greek word meaning to press, and piezoelectricity is pressure electricity. Piezoelectricity appears only in insulating solids. Although piezoelectricity can be generated in waxes which are solidified under an applied field, crystalline materials are, by far, the largest group of materials showing piezoelectricity. Piezoelectricity is distinguished from electrostriction, which is another effect which causes a solid dielectric to change shape on the application of a voltage, in that a reversal of the voltage reverses the sign of the resulting strain, whereas for electrostriction the strain is an even function of the applied voltage, and the strain does not reverse sign when the voltage is reversed. Electrostrictive effects are usually very feeble compared to piezoelectric effects but in the case of the ferroelectric materials, rochelle salt and barium titanate, they may be quite large.

All crystalline materials are anisotropic and do not have the same properties in all directions as do isotropic materials. Crystals can be divided into 32 classes on the basis of the symmetry they possess and, of these 32 classes, 20 possess the property of piezoelectricity and 12 do not. The criterion that determines whether a crystal is piezoelectric or not is its possession of a center of symmetry. A crystal possessing a center of symmetry cannot be piezoelectric because no combination of uniform stresses will produce a separation of the centers of gravity of the positive and negative charges and produce an induced dipole moment which is necessary for the production of polarization by stresses. Since a crystal is at once an electrical motor and an electrical generator, we have to consider the elastic and dielectric constants of the crystal as well as the piezoelectric constants. A crystal with no symmetry at all will have 21 elastic constants, 18 piezoelectric constants, and 6 dielectric constants. As the symmetry increases, the number of possible constants decreases, until the most symmetrical type of crystal, a cubic crystal, has only 3 elastic constants, 1 piezoelectric constant and 1 dielectric constant.

1.2 *Historical*

The piezoelectric effect was discovered experimentally by the brothers Pierre and Jacques Curie in the year 1880. By placing a weight on the surface of a crystal they produced a charge, measurable with an electrometer, which was proportional to the applied weight and hence discovered the direct effect. They found this effect in a considerable number of crystals including quartz, rochelle salt and tourmaline—crystals that are among those most used today. The converse piezoelectric effect, which deals with the motor property of the crystal, namely, producing a displacement when a voltage is applied, was predicted theoretically by Lippman in the following year 1881 and was verified by the Curies. Among the early investigators was Lord Kelvin, who suggested a molecular theory and produced a mechanical model of piezoelectricity; Pöckels, who made many determinations and contributed especially to the theory of the electro-optic effect in crystals; Duhem, whose formulation of piezoelectric principles was of fundamental importance; and finally Voigt, who systematized the work of his predecessors and whose monumental work, ***Lehrbuch der Kristallphysik***, contained most of what was known about piezoelectricity up to World War I.

The connection of piezoelectricity with atomic structure, while well established on a general basis, is in its infancy regarding predictions of magnitudes of piezoelectric constants and their connection with chemical composition. Among the more important contributions are those of R. E. Gibbs and Max Born, who predicted respectively piezoelectric constants for quartz and zinc blende that are within factors of 10 of the experimental values.

The piezoelectric effect remained more or less a scientific curiosity up to the time of World War I. During the war Prof. Langevin in Paris was requested by the French government to devise some way of detecting submarines. After trying several devices he finally found that piezoelectric quartz plates could be used for this purpose. His device consisted essentially of a mosaic of quartz glued between steel plates. This device has the property that, when a voltage is applied, the crystal will expand and send out a longitudinal wave. Similarly, when a wave strikes it, it will set the quartz in vibration and generate a voltage which can be detected by vacuum tube devices. Langevin did not get his device perfected until after the end of the war, but it has been used extensively as a sonic depth finder, and similar devices were used in the present war for detecting submarines.

In 1917, A. M. Nicolson at Bell Telephone Laboratories was experimenting with rochelle salt and he constructed and demonstrated loudspeakers, microphones and phonograph pickups using this crystal. He also controlled an oscillator by means of a crystal — in this case rochelle salt — and he has the primary crystal oscillator patent. In 1921, Cady at Wesleyan University showed that quartz crystals could be used to control oscillators and that much more stable oscillators can be obtained in this fashion. This use was a forerunner of the very wide application of crystals to control the frequency of military communication equipment which resulted in the use of more than 30,000,000 crystals in a single year. Quartz crystal oscillators using the GT crystal described in Chapter VI, produce the most stable oscillators and the best time-keeping systems that can be obtained. Both the Greenwich Observatory in England and the Bureau of Standards in Washington use such crystals in their primary standards.

Another large use for piezoelectric crystals is in producing very selective filter circuits. On account of the very high *Q* such crystals possess, they can be incorporated in filter circuits along with coils and condensers to give very discriminating filters. Such filters are used in all the high-frequency carrier systems and in the coaxial system for separating the simultaneous conversations that go over one pair of wires. For this purpose quartz was originally used, but a new synthetic crystal, ethylene diamine tartrate (EDT), has been developed which has low enough temperature coefficients and high enough stabilities to replace quartz for this application.

1.3 *Crystal Systems, Crystal Constants, and Motor Generator Effects*

Crystals are classified into 7 crystal systems and 32 crystal classes. The systems, as discussed in Chapter II, are determined by the shapes and dimensions of the smallest unit cells that surround a molecular configuration in such a manner that a simple translation of the unit cell along one of its axes by one unit length will cause it to surround a similar molecular configuration to that contained by the first cell. The edges of the unit cell are parallel to the crystallographic axes *a*, *b* and *c*, and the relative dimensions of the cell are the unit distances along these axes. The 32 crystal classes are determined by the elements of symmetry that are obtained in arranging the molecules within the seven elementary unit cells.

The most unsymmetrical type of system is the triclinic system, all three of whose crystallographic axes make oblique angles, and the lengths of the unit cells on the three axes are all unequal. In calculating the elastic constants of a triclinic crystal, as discussed in the appendix, it is more convenient to use a right-angled system of coördinates, rather than the crystallographic axes, and the question arises as to how these coordinates are to be related to the *a*-, *b*- and *c*-axes of the crystallographer. This question has been discussed by the Piezoelectric Crystal Committee of the

Institute of Radio Engineers under the chairmanship of Prof. W. G. Cady, and the system shown by Fig. 2.1 has been adopted. Here the z rectangular axis lies along the c crystallographic axis, the x rectangular axis lies in the plane of the a and c crystallographic axes and at right angles to the $c = z$ axis, while the y-axis is at right angles to the x- and z-axes in a right-handed system of coordinates. All the other systems are special cases of the most general case, as discussed in detail in Chapter II.

Depending on the crystal symmetries, crystals can have from 3 to 21 elastic constants, 0 to 18 piezoelectric constants and 1 to 6 dielectric constants. These are the constants referred to the x, y and z rectangular axes. If we wish to investigate the properties of crystals cut at oblique angles with respect to these axes, transformation equations, such as those discussed in the appendix, exist by means of which new elastic, piezoelectric, and dielectric constants can be calculated in terms of the constants for the new axes. These new constants are linear combinations of the fundamental constants. Conversely, in measuring the fundamental constants, it is often convenient to measure the properties of the oblique cuts and calculate the fundamental constants from the measured results. Oblique cuts are often of interest in themselves since special properties, such as low temperature coefficients, high electromechanical couplings, and freedom from secondary modes of motion, may often be obtained more easily in the oblique cuts than in cuts lying along the crystallographic axes.

Since a crystal is a motor generator, the constants of the crystal are going to vary depending upon the mechanical load attached to the crystal. For example, if the dielectric constant of a crystal is measured when it is clamped so hard that it cannot move, one obtains the so-called clamped dielectric constant of the crystal. If now the clamp has some compliance, some additional energy can be stored in the crystal in mechanical form and this results in an increase in the dielectric constant. The effect is greatest when the crystal is free to move, and one obtains the so-called "free" dielectric constant. The difference between the free and the clamped constant is determined by the electromechanical coupling factor for that crystal. This is defined as the square root of the ratio of the energy stored in mechanical form, for a given type of displacement, to the total input electrical energy obtained from the input battery. It is shown in Chapter V that this factor for a given mode of motion is equal to

$$k = \frac{d}{\sqrt{\frac{\epsilon^T}{4\pi} s^E}} \tag{1.1}$$

where d is the piezoelectric constant measuring the ratio of strain to field,

ϵ the dielectric constant and s the elastic compliance. In a converse manner, the elastic constant depends on the electrical condition obtained when the ratio of strain to stress is measured. If the electrical terminals are open-circuited, one obtains the elastic constant corresponding to a zero electric displacement (except for a minor class of crystals for which the direction of the electric displacement does not lie along the field), while if the terminals are short-circuited, one measures the constants for zero field. The ratio of these two constants and also the two dielectric constants are

$$\frac{s^E}{s^D} = \frac{\epsilon^T}{\epsilon^S} = \frac{1}{1 - k^2} \tag{1.2}$$

where ϵ^T is the constant stress (free) dielectric constant and ϵ^S the constant strain (clamped) dielectric constant. For most crystals with couplings, under 10 per cent, the difference is only about 1 per cent and is not too important. For ferroelectric crystals such as rochelle salt and potassium dihydrogen phosphate, however, the coupling may reach 90 per cent and the difference may be 5 to 1. Under these conditions it is essential to understand and measure the difference between these two types of constants.

1.4 *The Crystal Resonator and Transducer*

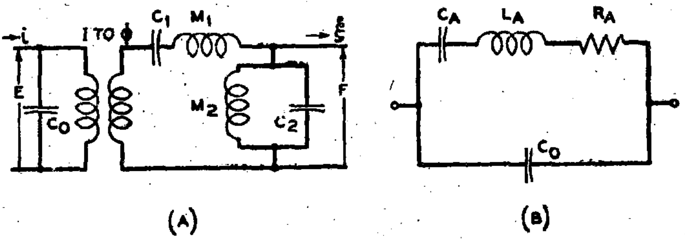
All of the applications of the piezoelectric effect depend on this motor generator action of the crystal. In the crystal resonator, the action drives the crystal itself in mechanical vibration and the mechanical vibration reacts back to control the electrical impedance of the crystal. As an electromechanical transducer the mechanical stress set up by the piezoelectric effect drives not only the mechanical elements of the crystal but also any other mechanical elements attached to the crystal surface. Phonograph pickups, headphones, loudspeakers, and in particular ultrasonic transducers are examples of this use. In the frequency range above about 10 kilocycles, piezoelectric crystals form the best means of transferring electrical into mechanical energy, and the last three chapters of the book are devoted to a description of these methods and results that have been obtained with them.

In analyzing the performance of a crystal for these functions, it is very convenient to obtain an equivalent electrical circuit which represents the electrical and mechanical properties of the crystal. For a crystal that is free on one end and drives a load on the other, a circuit which represents the performance of such a crystal near its resonant frequency is shown by Fig. 1.1A. Here C_0 is the static capacity of the crystal, 1 to φ is a constant that measures the force exerted by the crystal for a given applied voltage,

C_1 a compliance equal to $8/\pi^2$ times the static compliance of the crystal, M_1 a mass equal to $\frac{1}{8}$ the total mass of the crystal, C_2 a compliance equal to $\frac{1}{2}$ the static compliance of the crystal, and M_2 a mass equal to $2/\pi^2$ times the total mass of the crystal. With these values the two networks resonate at the natural resonant frequency of the crystal given by

$$\frac{\omega l}{V} = \pi \quad \text{or} \quad f = \frac{v}{2l} = \frac{1}{2l}\sqrt{\frac{1}{M_0 C_0}} = \frac{1}{2\sqrt{MC}} \tag{1.3}$$

where M_0 and C_0 are the mass and compliance per unit length and M and C the total mass and compliance of the crystal. Using this simple circuit the effect of adding mechanical units on the driving end of the crystal is easily analyzed.



(A) (B)

FIG. 1.1. Equivalent electromechanical and electrical circuits for a piezoelectric crystal.

If the crystal is free on both ends, the driving end of Fig. 1.1A can be short-circuited and the equivalent circuit of Fig. 1.1B results. The performance of a crystal resonator in an oscillator or filter can be analyzed by inserting this network in the place of the crystal. In quartz resonators the inductance L_A varies from the order of 0.1 henry with crystals vibrating at 2500 kc to 100 henries or more with low-frequency resonators. The synthetic crystals ADP and EDT have considerably lower values of inductance for the same size and frequency crystals, on account of the much higher electromechanical coupling. The capacitance C_A is usually in the order of a few tenths to 10 micromicrofarads. It is this enormous ratio of L_A to C_A together with the very low value of R (high Q) that gives the crystal its ability to control the frequency of an oscillator within narrow limits. The Q of a crystal in laboratory experiments[1] has been measured as high as 6,000,000 and, even in commercially mounted crystals which have to be securely held in order to stand extraneous knocks, Q's in the order of several hundred thousand are common.

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[1] Van Dyke, K. S., "Vibrational Modes of Low Decrement for a Quartz Ring," *Phys. Rev.*, Vol. 53, p. 943, 1938.

In every piezoelectric oscillator circuit, the crystal acts fundamentally as a resonator. It does not generate energy, but by the electrical reactions of its vibrations it determines the alternating potential on the grid of the oscillator and controls it over a narrow frequency range. The equivalent circuit of the crystal has a frequency of resonance for which the impedance is low and a frequency of anti-resonance for which the impedance is high.

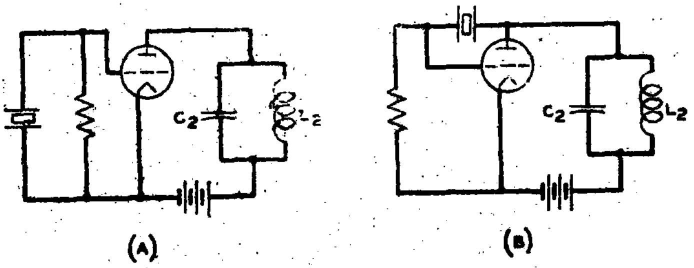

FIG. 1.2. Pierce-Miller and Pierce circuits for crystal oscillators.

In the more common form of oscillators, such as the Pierce circuits illustrated by Fig. 1.2, the frequency of oscillation comes between the resonance and anti-resonance frequency, although nearer the resonance. In later oscillators, such as the Meacham bridge oscillator, the frequency of oscillation coincides with the natural resonance frequency of the crystal.

1.5 *Important Piezoelectric Crystals*

In all, probably over five hundred crystals have been tested and a fair share of them have piezoelectric responses. Of these, however, only a few have come into practical use. Before World War II the only crystals that were at all widely used were quartz, rochelle salt and tourmaline. Quartz was used in all oscillator and filter applications, rochelle salt in most low-frequency transducer applications and tourmaline was used solely for measuring hydrostatic pressures. Stimulated by the need for a piezoelectric transducer for underwater sound applications that was more stable and less temperature sensitive than rochelle salt, considerable work was done during World War II in searching for new piezoelectric crystals. This resulted in the discovery and application of ammonium dihydrogen phosphate (ADP) to underwater sound transducers. On account of its freedom from water of crystallization (and hence dehydration), the higher temperature it will stand (up to 100°C), and the greater mechanical stability, this crystal largely displaced rochelle salt and even other types of electromechanical transducers for underwater sound applications. It appears likely that it may replace rochelle salt for a number of peacetime applications as well.

Up to the present time quartz has been practically the only crystal suitable for the precise control of frequency in transmitting, monitoring, and receiving circuits, and in the production of very selective circuits. Quartz, which is the most abundant of natural crystals, is chemically stable at all ordinary temperatures and has very low internal losses. Furthermore, by cutting the crystal at various oblique orientations with respect to the crystallographic axes, it is possible to make resonators with very low temperature coefficients of frequency, and freedom from effects of other modes of motion. These characteristics of quartz have led to its exclusive use for primary frequency standards and as a means for obtaining very selective filters.

In the latter use, fairly large-sized crystals up to 5 centimeters in length are required. As the war progressed and more and more quartz was used in producing oscillator crystals, large-sized crystals became more difficult to obtain. With the end of the war the supply of large-sized crystals became insufficient to satisfy the needs of the telephone systems. Fortunately a study of the properties of synthetic crystals carried out during the last ten years at Bell Laboratories had resulted in discovering two new crystals which were capable of meeting the requirements necessary for filter crystals. These were two monoclinic sphenoidal crystals, ethylene diamine tartrate (EDT) and dipotassium tartrate (DKT). Low-temperature cuts in both crystals and higher electromechanical couplings are possible than exist in quartz. Of these crystals EDT has no water of crystallization, will stand a temperature of 120°C, and is easier to grow than DKT. The Western Electric Company has established a growing and processing plant for this crystal in Allentown, Pa., and it is planned to incorporate them in the high-frequency carrier and coaxial filters of the long-distance telephone systems. The properties of these crystals are described in Chapter IX.

Rochelle salt ($NaKC_4H_4O_6\text{-}4H_2O$) is the most strongly piezoelectric crystal at room temperatures. This is due to the fact that it becomes ferroelectric in the temperature range from $-18°C$ to $+24°C$. Its dielectric properties are strikingly analogous to the ferromagnetic properties of iron. Below a certain temperature, which is called the Curie temperature, it exhibits dielectric hysteresis and has a dielectric constant that becomes very large for weak fields, at the Curie points. Unlike ferromagnetic materials, rochelle salt has a lower Curie temperature as well as an upper one. Potassium dihydrogen phosphate (KDP) is another ferroelectric type crystal that has only one Curie temperature, 121°K, above which it is non-ferroelectric and below which it is ferroelectric.

These two cases are discussed in Chapter XI and it is there suggested that both effects are due to a hydrogen bond dipole caused by the displacement of the hydrogen nucleus from the midpoint between the two oxygens. KDP has a symmetrical bond and, when a factor

$$A = \frac{N\mu^2\beta}{kT\left(1 - \frac{4\pi}{3}\gamma\right)} \tag{1.4}$$

becomes greater than one, the crystal becomes ferroelectric. In this equation N is the number of dipoles per cc, μ the dipole moment, β the Lorentz factor connecting the polarization with the internal field, k Boltzmann's constant, T the absolute temperature, and γ the polarizability in the absence of the hydrogen dipole. Rochelle salt has two sets of dissymmetrical bonds, and the lower Curie temperature is caused by the hydrogen nucleus freezing in the lower potential wells as the temperature is lowered. Although these effects are interesting scientifically, they detract from the usability of the crystal since the elements are so field and temperature sensitive. Considering this and the fact that rochelle salt tends to become dehydrated and that it disintegrates at 55°C, one can understand the need for a new crystal for transducer use that is free from these defects. This need is largely filled by ADP ($NH_4H_2PO_4$), as mentioned previously.

1.6 *Miscellaneous Applications*

In addition to the use of piezoelectric crystals in resonators and transducers, two second-order effects have recently become of importance. These are the electro-optical and piezo-optical effects which are caused respectively by the change in dielectric constant due to an applied voltage and the change in dielectric constant due to an applied stress. These effects were first investigated theoretically and experimentally by Pöckels. It was not, however, until the advent of ADP and KDP that any crystal with large enough electro-optical and piezo-optical constants to be of interest, were available. With these crystals light modulators can be obtained which work on voltages of 2000 volts or less. Furthermore, since the electro-optical effect depends on a change in the dielectric constant with voltage and the dielectric constant is known to be independent of frequency up to at least 10^{10} cycles, it appears likely that the electro-optical constant should also be independent of frequency up to this value.

Billings[2] has recently proposed the use of the electro-optical effect of an

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[2] Billings, B. H., "A tunable narrow band optical filter," J. Opt. Soc. Amer. Vol. 37, No. 10, Oct. 1947.